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FINAL REPORT

THE SPECIATION and BIOACCESSABILITY OF ANOMALOUS LEAD CONCENTRATIONS IN SOILS FROM THE HERCULANEUM COMMUNITY—HERCULANEUM, MISSOURI.

May 24, 2005

FOR

Black & Veatch

U.S. Environmental Protection Agency
Region VII

BY

DR. JOHN W. DREXLER
LABORATORY FOR ENVIRONMENTAL AND GEOLOGICAL STUDIES
UNIVERSITY OF COLORADO
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1.0 INTRODUCTION

On September, 2004 Black and Veatch, on behalf of U.S. Environmental Protection Agency (USEPA) requested the Laboratory for Environmental and Geological Studies (LEGS), at the University of Colorado to undertake a lead characterization study on residential soils from the Herculaneum, Missouri area. In response to this request a mineralogical and geochemical study was conducted on community and facility media in order to characterize the form(s) of lead, and their bioaccessability . Samples were acquired from the Doe Run lead smelter (herein referred to as Facility), roadside soils, along with residential soils and household dusts by representatives of the USEPA. Samples of atmospheric dust were also provided by the State of Missouri. A site map, with some sample locations and selected demographics are indicated on Figure 1.

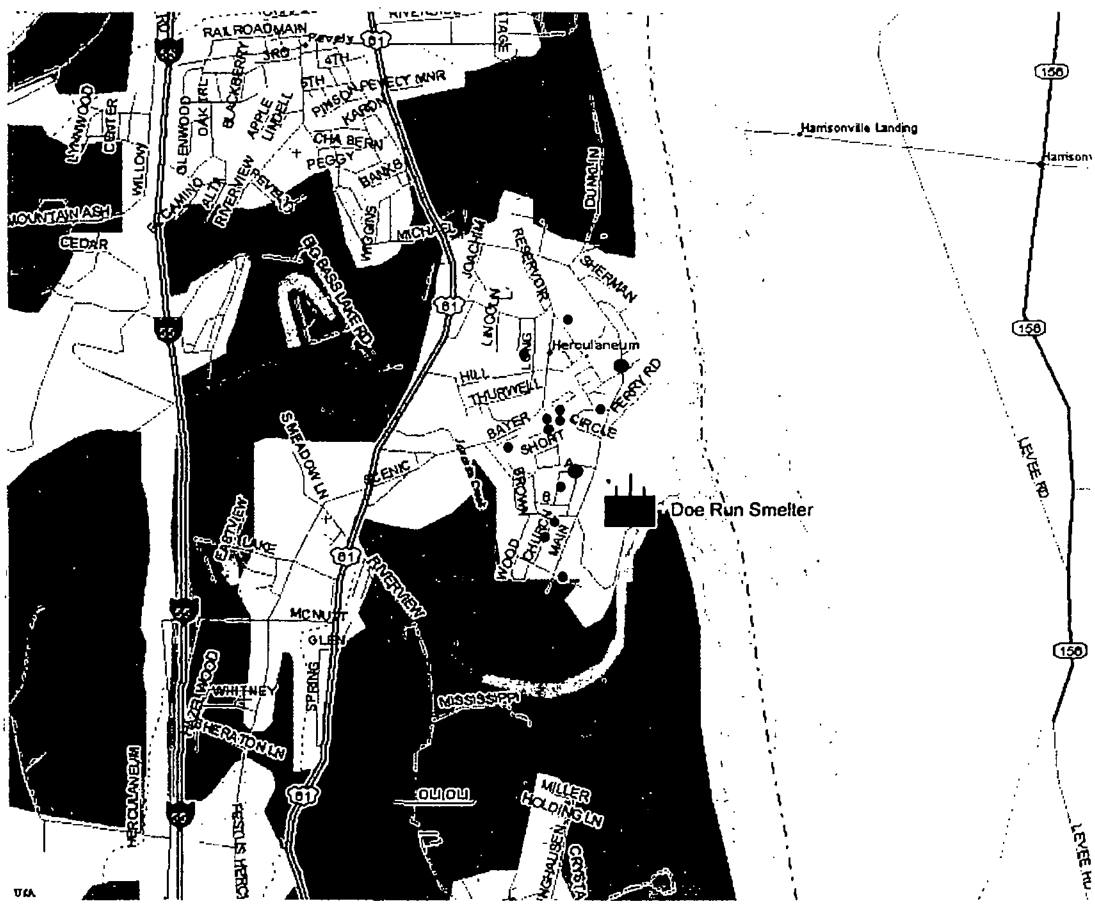
2.0 HISTORICAL BACKGROUND

The Herculaneum Smelter facility is located in Herculaneum, Jefferson County, Missouri. It is owned and currently operated by the Doe Run Mining Company (approximately 30 miles south of St. Louis, MI.). The Herculaneum smelter facility is currently active and has been operating at its present location since 1892. It produces 250,000 tons of refined lead per year and approximately an equal volume of waste. Concentrate is transported to the smelter by truck and rail from eight lead mines owned by Doe Run in the historical, Viburnam Trend. Facilities are likely to impact Herculaneum residential corridors, as the facility resides in the small community (~2800 people) with an additional 10,000 residence within a five mile radius. The US

Department of Health and Human Services, 2002 found that 28% of the children in the community have blood lead levels exceeding the CDC guidance level of 10 μg/dl, and that population increases to 45% as one moves east of State highway 61.

The facility consists of a blast and dross furnace, a sinter facility, a large (24 acre) slag storage pile, and a sulfuric acid facility.

Figure 1. Herculaneum Site Map.



Red circles are residential soil and dust samples, green circles are atmospheric dust stations.

3.0 FIELD SAMPLING ACTIVITIES

Black & Veatch Special Projects Corp. (BVSPC) was tasked by the U.S. Environmental Protection Agency, Region VII, to complete a Site Investigation at the Herculaneum Lead Smelter (HLS) in Herculaneum, MO. Field activities began on August 23rd, 2004 and were completed on September 2, 2004.

The purpose of this site investigation was to obtain specific samples to 1) determine the sources of lead in residential contaminated soils and interior house dusts surrounding the HLS, 2) determine the apportionment of lead species in the residential contaminated soils and interior house dust, and 3) determine the bioavailability of lead species found near the smelter. For the purpose of this study, the lead concentrations in residential surface soils and interior house dust needed to be 1,200 parts per million (ppm) or greater. Note that not all of the interior house dust samples showed a 1,200 ppm lead concentration based upon the XRF result. Nonetheless, these samples were utilized in this study to ensure that 1.75 pounds of residential house dust required for the in-vivo study.

3.1 Overview of Vacuum Bag Interior Residential Dust Sampling

A total of 10 interior house dust samples were collected from residences within a 1.0 mile radius of the HLS site. Vacuum bag interior residential dust samples were collected from locations identified through previous site investigations of having a residential surface soil lead concentration of 1,200 ppm or greater and those locations where residential yard remediation (excavation) had not occurred. The interior house dust samples are represented by the material collected in the resident's vacuum bag. The procedure for the collection and preparation of vacuum bag dust samples was as follows:

1. Access was obtained once permission from the owner/resident was granted.
2. Sampler donned a clean pair of gloves and removed vacuum bag from vacuum.
3. Vacuum bag samples were immediately placed into zip lock bags and labeled.
4. Samples were returned to EPA trailer and preliminary XRF readings were collected to

confirm that lead concentrations for the vacuum bag samples were 1,200 ppm or greater.

5. Samples were screened with the XRF three individual times, per standard operating procedures, using the NITON 300/700 Series XRF Analyzer.
6. Vacuum bags were then removed from zip lock bags and cut open with scissors.
7. The contents of the vacuum bag was then removed and placed in a No. 60 mesh sieve.
8. Samples were sieved into a clean aluminum pan.
9. After sieving was completed, samples were transferred from the aluminum pan into a new zip lock bag, labeled, and a Final XRF screening result was recorded.

The original *Field Sampling Plan* (BVSPC, 2004a) provided that 6 samples would be collected of interior vacuum bag dust. However, the USEPA approved the collection of four additional dust samples to obtain the weight requirement of 1.75 lbs for the study. Interior house dust vacuum bag samples and the corresponding Final XRF screening results are listed below in

Table 3.1.

Table 3.1. Final XRF Screening Results Vacuum Bag Interior Dust Samples	
Address / Sample ID	**XRF Lead Screening Results (ppm)**
HLS-VBD-430 Hill-EPA	1460 ± 140 1480 ± 140 1230 ± 160
HLS-VBD-511 Long-EPA	1400 ± 120 1000 ± 94 1070 ± 93
HLS-VBD-835 Cross-EPA	11,800 ± 590 5800 ± 570 16,800 ± 790
HLS-VBD-552 Reservoir-EPA	933 ± 85 858 ± 73 756 ± 70
HLS-VBD-515 Thurwell-EPA	645 ± 70 586 ± 330 583 ± 66
HLS-VBD-306 Main-EPA	534 ± 53 368 ± 49 766 ± 74
HLS-VBD-774 Circle-EPA	1370 ± 140 1430 ± 130 1650 ± 160
HLS-VBD-785 Circle-EPA	2370 ± 150 1990 ± 140 2020 ± 150
HLS-VBD-905 Church-EPA	2780 ± 200 2600 ± 230 1680 ± 140
HLS-VBD-320 Curved-EPA	1860 ± 130 1560 ± 160 1820 ± 140

The XRF results showed that the interior house dust from 552 Reservoir, 515 Thurwell, and 306 Main having lead concentrations less than the in-vivo study requirement of 1,200 ppm lead. However, based upon the 1.75 pounds of dust that is required for the in-vivo study, it is likely that the vacuum bag samples collected will be utilized to create a composite sample meeting the weight and lead concentration requirements for the in-vivo study.

The vacuum bag dust samples were submitted to the University of Colorado (CU) for total lead analysis, in-vitro bioavailability analysis, and lead speciation. Upon a decision from the EPA regarding the study results from CU, the interior house dust vacuum bag samples will be prepared for shipment to the University of Missouri at Columbia (MU) for the in-vivo bioavailability study.

3.2 Overview of Residential Surface Soil Sampling

Residential Surface Soil Sample Collection

Once residential access had been obtained, 10 soil samples were collected from residences located within a 1.0 mile radius of the HLS site. Surface soil sample locations were pre-determined based upon residential surface soil lead concentrations recorded from previous site investigations. During field activities, the EPA requested that BVSPC also collect two additional samples from residential yards identified from the ongoing recontamination study (824 Brown and 928 Church). The residential surface soil collected from these two locations will be subjected to the in-vitro bioaccessability study, lead speciation, and lead analysis; however, the surface soil will not be utilized in the in-vivo study to be completed at a later date by MU.

In accordance with the *Field Sampling Plan* (BVSPC, 2004a), residential yards were typically divided into four quadrants, except for smaller yards where it was appropriate to identify only two quadrants. One surface soil composite sample was collected from four or five different locations within each quadrant. Residential surface soil sample locations were chosen based upon XRF results identified through previous site investigations of having a lead concentration of 1,200 ppm or greater. As previously mentioned, surface soil possessing at least 1,200 ppm is required for the in-vivo study pursuant to the study methodology but not necessarily according to the in-vitro study methodology. Further, the in-vitro study, discussed herein, has been conducted to ascertain the bioaccessibility the lead species identified in the residential yard surface soils. Therefore, if a residential yard was identified by four quadrants (F1, F2, F3, and F4) but results from a previous investigation indicated only quadrant F2 and quadrant F3 had lead concentrations 1,200 ppm or greater, then only those specific quadrants were used to create the sample for this study and ultimately the in-vivo study. However, variations were required at the time of the field investigation in order to fulfill the study objectives. For example, the XRF screening results for 300 St. Louis, 515 Thurwell, and 351 Short show lead concentrations below the 1,200 ppm study target concentration; however, the surface soil collected from these residents is being utilized in this study for several reasons. The location 300 St. Louis is located 0.91 miles from the smelter making it the farthest from the HLS site. The location 515 Thurwell was chosen in lieu of 507 Thurwell because there was no answer at the door of 507 Thurwell after repeated attempts to speak to the resident to obtain access. Further, a previous investigation at the 515 Thurwell address indicated the F1 quadrant contained more than 4,000 ppm lead while the B2 quadrant contained over 1,000 ppm lead. Realizing a combination of those two quadrants would yield lead concentrations most likely at or above the 1,200 ppm lead goal. Likewise regarding the location 351 Short; a previous investigation indicated quadrant B1 contained lead concentrations over 3,000 ppm and the B2 quadrant contained 1,400 ppm lead. While the XRF screening result for lead obtained during this field study revealed lead concentrations less than the study target, the final list of residents sampled during this investigation was highly dependent upon whether the home owner granted property access to BVSPC personnel and the number of individual residents who previously refused excavation and remediation of their yards.

Surface soil samples were collected from the top one inch of the soil. Often, the first inch of soil bound with the vegetative mat (typically grass). Where this occurred, the soil was removed from the vegetation in an effort to capture the very top one inch of surface soil. BVSPC collected several pounds of soil from each residence to ensure that there was a sufficient amount of material to meet all study and analysis requirements.

Residential Surface Soil Sample Preparation

Once the quadrant sample was collected, each individual quadrant sample was screened for its lead concentration using the NITON XRF analyzer. Those samples possessing a lead concentration from 1,200 ppm and greater were then combined and thoroughly homogenized to create one sample representing each resident. In some instances, the surface soil XRF screening results indicated lower than expected lead concentrations. These surface soil samples were contained in a zip-lock baggie, labeled, and are being stored in a box in the EPA trailer in Herculaneum.

For each homogenized residential surface soil sample prepared, approximately 7-8 oz (weight before drying) of soil was removed from the mixture. Additionally, approximately 1.7 to 2.0 pounds of the soil was removed from the mixture, placed into a zip-lock baggie, labeled, and set-aside in a clean, dry cardboard box. The smaller sample (7-8 oz.) was placed into an aluminum pie pan, and dried at 300 degrees Fahrenheit using a toaster oven. Once the sample was dried enough to easily sieve, the soil was sieved into an aluminum pie pan using a No. 10 sieve. The surface soil sample was then transferred into a zip-lock baggie and labeled.

Each of the prepared residential surface soil samples weighing between 7 and 8 ounces were submitted to CU for analysis. The 1.7 to 2.0-pound, homogenized, surface soil sample was transferred to the EPA Region VII laboratory where the material is being stored under custody pending the in-vitro bioavailability results, the total lead analytical results, and the speciation results. Based upon the CU study results, resident(s) surface soil will be identified for the in-vivo bioavailability study to be completed by MU.

Table 3.2 provides a summary of the residential surface soil samples collected during this site investigation. The homogenized, prepared surface soil samples were subjected to a Final XRF screening. The Final XRF screening results are listed in Table3.3. Additionally, BVSPC collected Final XRF screening results of the bulk (1.7 to 2.0 pounds) surface soil material. The XRF screening results of the bulk surface soil are listed in Table 3.4.

Table 3.2. Summary of Residential Surface Soil Samples				
Address	**Quadrants Used**	**Sample Destination**	**Weight**	**Date of Sample Collection**
835 Cross	F1, F2, B2	EPA Casteel Drexler	1 lb 1 lb 13 oz 4oz	8.26.04
515 Thurwell	F1, F2	EPA Casteel Drexler	1 lb 1 lb 15 oz 4 oz	8.26.04
425 Hill	B1, B2, F1	EPA Casteel Drexler	1 lb 1 lb 15 oz 6 oz	8.26.04
511 Long	F1, B1	EPA Casteel Drexler	1 lb 1 lb 15 oz 6 oz	8.27.04
517 Long	F1, B1	EPA Casteel Drexler	1 lb 1 lb 13 oz 6 oz	8.27.04
351 Short	F1, F2	EPA Casteel Drexler	1 lb 1 lb 13 oz 5.5 oz	8.27.04
430 Hill	F1, F2, B1	EPA Casteel Drexler	1 lb 2 lbs 5 oz	8.30.04
552 Reservoir	F1, F2, B2	EPA Casteel Drexler	1 lb 1 lb 12 oz 5 oz	8.30.04
306 Main	F1, B1, B2	EPA Casteel Drexler	1 lb 2 lbs 4.5 oz	8.31.04
300 St. Louis	F1, Play Area	EPA Casteel Drexler	1 lb 1 lb 14 oz 4 oz	8.31.04
824 Brown (recontaminati on study)	F1, F2	EPA Casteel Drexler	1 lb 11 oz 4 oz	8.31.04
928 Church (recontaminati on study)	F1, F2	EPA Casteel Drexler	1 lb 1 lb 4 oz	8.31.04

Table 3.3. Final XRF Screening Results for Residential Surface Soil Samples Weighing 7 – 8 oz.	
Address	**Lead XRF Screening Results (ppm)**
HLS-SS-306 Main-CU	2030 ± 210 2040 ± 200 2170 ± 190
HLS-SS-300 St. Louis-CU	436 ± 82 507 ± 80 406 ± 85
HLS-SS-824 Brown-CU (Recontamination Study)	750 ± 95 793 ± 110 800 ± 100
HLS-SS-928 Church-CU (Recontamination Study)	425 ± 81 320 ± 79 394 ± 91
HLS-SS-835 Cross-CU	2270 ± 190 2020 ± 190 1960 ± 180
HLS-SS-515 Thurwell-CU	880 ± 100 856 ± 100 852 ± 110
HLS-SS-425 Hill-CU	1410 ± 150 1310 ± 110 1410 ± 140
HLS-SS-511 Long-CU	1460 ± 140 1450 ± 150 1440 ± 150
HLS-SS-517 Long-CU	1980 ± 170 1850 ± 180 1950 ± 170
HLS-SS-351 Short-CU	481 ± 74 512 ± 73 498 ± 73
HLS-SS-552 Reservoir-CU	3710 ± 270 3360 ± 250 2980 ± 430
HLS-SS-430 Hill-CU	2050 ± 180 1710 ± 190 2190 ± 190

Table 3.4. Final XRF Screening Results for Residential Bulk Surface Soil Samples	
Address	**Lead XRF Screening Results (ppm)**
HLS-SS-306 Main-MU	1700 ±180 2000 ± 180 1420 ± 160
HLS-SS-300 St. Louis-MU	368 ± 73 427 ± 73 419 ± 74
HLS-SS-835 Cross-MU	1660 ± 290 1580 ±130 1500 ±160
HLS-SS-515 Thurwell-MU	854 ±110 630 ± 110 682 ± 100
HLS-SS-425 Hill-MU	1340 ±140 1190 ±140 1050 ±120
HLS-SS-511 Long-MU	1160 ± 120 1210 ±140 1040 ± 170
HLS-SS-517 Long-MU	1510 ± 150 1250 ± 170 1390 ± 130
HLS-SS-351 Short-MU	616 ± 83 572 ± 93 485 ± 81
HLS-SS-552 Reservoir-MU	3170 ± 230 3160 ± 230 2840 ± 250
HLS-SS-430 Hill-MU	1410 ± 180 1360 ± 170 1590 ± 140

3.3 Sample Location Distance from the Herculaneum Lead Smelter

Table 3.5 indicates the distance of each residence from the smelter location. Note that soil samples from 928 Church and 824 Brown were collected as part of a recontamination study and were sent with other samples to the University of Colorado at Boulder for speciation and total lead analysis. They will also be used as part of the in-vitro study.

Table 3.5. Residential Surface Soil and Dust Sample Location Information

Address	Media Sampled	Distance From Smelter
425 Hill	Soil	0.57 miles
928 Church	Soil	0.23 miles
430 Hill	Soil/Dust	0.56 miles
515 Thurwell	Soil/Dust	0.58 miles
552 Reservoir	Soil/Dust	0.47 miles
511 Long	Soil/Dust	0.51 miles
835 Cross	Soil/Dust	0.26 miles
306 Main	Soil/Dust	0.90 miles
905 Church	Dust	0.20 miles
785 Circle	Dust	0.27 miles
774 Circle	Dust	0.30 miles
320 Curved	Dust	0.18 miles
300 St. Louis	Soil	0.91 miles
517 Long	Soil	0.50 miles
351 Short	Soil	0.30 miles
824 Brown	Soil	0.40 miles

3.4 Sample Collection at the Herculaneum Lead Smelter

Samples were collected from inside the HLS facility, slag piles, and from the primary and secondary transport haul routes. Samples collected from inside the smelter facility included dust samples from various bag houses as well as a sample from an electrostatic precipitator. In accordance with the Final Work Plan (BVSPC, 2004c), grab samples were collected from specific bag houses to represent primary stack emissions, sinter plant stack emissions, and bag house material (BVSPC, 2004c).

In order to comply with Doe Run's company policies and regulations regarding safety practices, BVSPC was not allowed to directly collect samples. A Doe Run facility Operator collected these samples under the direct supervision of BVSPC, who was present for all sampling. Table 3.6 shows the description, location, and sample representation of all samples collected from within the HLS facility.

Grab samples were collected from primary and secondary haul routes used by trucks to deliver lead concentrate to the HLS facility (see Table 3.6). These samples were collected randomly along the haul routes from several areas where road dust material had accumulated. Grab samples were collected in three to five different locations to create a composite sample representing each specific haul route. The material was collected using a clean gardening trowel and placed in a clean, new, labeled zip lock baggie.

Grab samples were also collected from the slag piles located at the HLS site. Grab samples were collected from two different slag pile locations to represent two individual slag pile samples. Several grab samples were collected to create one composite sample representing two distinct locations from the slag pile.

Samples from two different lead concentrate transport vehicles were collected upon their arrival at the off-loading area. Samples of the lead concentrate were obtained immediately after the material was transferred from the transport vehicle into the HLS facility's hopper/ off-loading area. Three to five grab samples were collected from two different transport trucks to create two individual composite samples of lead concentrate. These samples were collected using a clean gardening trowel.

Grab samples described above were collected using a clean gardening trowel. The BVSPC sampler donned a clean pair of gloves to collect sample. Samples were placed in labeled zip lock bags.

Table 3.6. Samples Collected from HLS Site

Sample ID	Sample Description	Sample Location and Representation
HLS-RD-1-CU	Road dust sample	Near HLS facility, between concentrate off-loading area and truck decontamination area. Represents primary haul route sample.
HLS-RD-2-CU	Road dust sample	Grab samples collected from different locations on Station Street. Represents secondary haul route sample.
HLS-RD-3-CU	Road dust sample	Grab samples collected from different locations at the intersection of Main Street and Ferry Street. Represents secondary haul route sample.
HLS-RD-4-CU	Road dust sample	Grab samples collected from different locations near the East bridge abutment located at Joachim Street and Brown Street. Represents primary haul route sample.
HLS-TC-1-CU	Truck lead concentrate	Truck off-loading area
HLS-TC-2-CU	Truck lead concentrate	Truck off-loading area
HLS-SLAG-1	Slag	Slag pile on HLS site
HLS-SLAG-2	Slag	Slag pile on HLS site
HLS-CBH-1	Dust	Cooler Bag House – represents primary stack emissions sample.
HLS-BH5-1	Dust	Bag House 5 – represents Bag House sample.
HLS-BH3-1	Dust	Bag House 3 – represents sinter plant emissions sample.
HLS-BH7-1	Dust	Bag House 7 – represents Bag House sample.
HLS-ESP-1	Dust	Electrostatic Precipitator – represents sinter plant emissions sample.
HLS-BH6-1	Dust	Bag House 6 – represents primary stack emissions sample.

3.5 Air Monitoring Filter Media Collection

The *Field Sampling Plan* (BVSPC, 2004a) identified the collection of air monitoring filters from the Herky Broad 57 Street and Herculaneum High School air monitoring locations. The Missouri Department of Natural Resources (MDNR) maintains specific air monitoring locations in Herculaneum. BVSPC and the EPA coordinated with the MDNR for the release of air monitoring filters representing time before and after August 2002. Through various conversations between BVSPC, EPA, and the MDNR, it was determined that air monitoring samples from the Bluff Station would replace samples from the Herculaneum High School. Arrangements were made for the MDNR to directly provide CU with specific air monitoring filter samples via overnight delivery. The particles that had been captured on the air monitoring filter media were subjected to speciation and in-vitro bioavailability analysis.

4.0 LEAD SPECIATION

Ten samples from the Doe Run facility (Table 4.1), twenty-six samples from the surrounding community (Table 4.2.) And ten atmospheric dust samples (Table 4.3) were speciated for lead using electron microprobe (EMPA) techniques. Methodologies used for sample preparation, data collection, and data synthesis are briefly described below, for more detail see the Metal Speciation Standard Operating Procedure, Appendix I.

4.01 Methodology

Metal speciation was conducted on a JEOL 8600 electron microprobe (EMPA), operating at 15Kv (accelerating voltage) and 15-20 NanoAmp current, at the Laboratory for Geological Studies at the University of Colorado following the laboratory's SOP. One exception was made in the SOP, in that the samples were not sieved to <250 µm, as is most common for bioavailability determinations, but the 2mm fraction was used in order to be consistent with previous site studies in which lead sourcing and/or apportionment are the primary task (USEPA 1996, 1999, 2001 and CDPHE, 1998). The samples were all air dried and prepared for speciation analysis as outlined in the SOP . A combination of both an Energy Dispersive Spectrometer (EDS) and a Wavelength Dispersive Spectrometer (WDS) were used to collect x-ray spectra and determine elemental concentrations on observed mineral forms. All quantitative analyses are based on certified mineral and metal standards using a Phi Rho Z correction procedure. Representative backscatter photomicrographs (BSPM) illustrating sample characteristics were acquired.

Data from EMPA will be summarized using three methods. The first method is the determination of FREQUENCY OF OCCURRENCE (F). This is calculated by summing the longest dimension of **all** the lead-bearing forms observed and then dividing each form by the total length for **all** forms. Equation 1.0 will serve as an example of how to calculate the frequency of occurrence for an lead- bearing compound.

F_{Pb} - Percent frequency of occurrence of lead in a single form.

PLD - An individual particle's longest dimension (microns)

$$F_{Pb\ in\ form\text{-}1} = \frac{\sum (PLD)_{form\text{-}1}}{\sum (PLD)_{form\text{-}1} + \sum (PLD)_{form\text{-}2} + \sum (PLD)_{form\text{-}n}} \qquad \text{Eq. 1.0}$$

$$\%F_{Pb \text{ in form-1}} = F_{Pb \text{ in form-1}} * 100$$

Thus, the frequency of occurrence of lead in each form (F_{Pb}) is calculated by summing the longest dimension of all particles observed for that form and then dividing each form by the total of the longest dimensions for all forms. The data generated illustrate which lead-bearing form(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report determines the Percent RELATIVE MASS lead (RM_{Pb}) of a form. These data are calculated by substituting the PLD term in the equation above with the value of RM_{Pb}. This term is calculated as defined below.

RM_{Pb} - Percent relative mass of lead in a form

SG - Specific gravity of a form (g/cm^3)

ppm_{Pb} - Concentration in mg/kg of lead in form (see Table 1.0A, Appendix I)

$$\% RM_{Pb} = \%F_{Pb} * SG * ppm_{Pb} \qquad \text{Eq. 2.0}$$

The advantage in reviewing the RELATIVE MASS lead determinations is that it gives one information as to which lead-bearing form(s) in a sample are likely to control the total bulk concentration for lead. As an example, Form-1 may, by relative volume(%F), contribute 98% of the sample volume, however it has a low specific gravity and contains only 1000 ppm lead, whereas Form-2 contributes 2% of the sample, has a high specific gravity and contains 850000 ppm of lead. In this example it is Form-2 that is the dominant source of lead to the sample.

The third calculation is to determine the BIOACCESSABLE MASS lead (Bio_{Pb}). For this calculation the same procedure as outlined above is used however, the original particle-count data set has been screened to use **only** liberated and cemented particles less than 250 microns in size. The reasoning behind these calculations are: 1) A particle greater than 250 microns is not bioaccessable. It will not adhere to clothes or hands. 2) A particle of lead that is enclosed within another mineral is considered far less bioaccessable, as one would need to dissolve the outer mineral or disaggregate the enclosed lead particle to make it available. 3) Finally, these data are considered likely to better reflect results observed from *invitro* or *invivo* studies.

4.02 Point Counting

Lead-bearing particle counts are made by traversing each sample from left-to-right and top-to-bottom. The amount of vertical movement for each traverse would depend on magnification and

CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings should be used. One ranging from 40 to 100X and a second from 300 to 600X. The last setting will allow one to find the smallest identifiable (1-2 micron) forms.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of lead-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours or 100 total particles will be spent per sample. This criteria is chosen to optimize the cost of EMPA analyses versus a statistically meaningful particle count.

Table 4.1. Doe Run Facility Samples.

Sample Id	Source	<250μ Pb mg/kg	Bulk >2mm Pb mg/kg
Slag-1	Slag	30488	20248
Slag-2	Slag	37906	24131
TC-1	Concentrate	374192	325581
TC-2	Concentrate	379797	319619
CBH-1	Cooler Baghouse	343470	NA
ESP-1	Electrostatic Precipitator	281830	NA
BHG-3	Baghouse	335158	NA
BHG-5	Baghouse	483095	NA
BHG-6	Baghouse	444480	NA
BHG-7	Baghouse	352684	NA

NA= No material > 250 micron was found.

Table 4. 2. Residential Media samples.

Sample ID		<250μ Pb mg/kg	Bulk >2mm Pb mg/kg
430-D- Hill	Interior Dust	1940	NA
320-D-Curved	Interior Dust	2542	NA
515-D-Thurwell	Interior Dust	1272	NA
835-D-Cross	Interior Dust	24651	NA
552-D-Reservior	Interior Dust	2478	NA
905-D-Church	Interior Dust	3852	NA
306-D-Main	Interior Dust	2787	NA
511-D-Long	Interior Dust	2394	NA
785-D-Circle	Interior Dust	4395	NA
774-D-Circle	Interior Dust	2468	NA
RD-1	Roadside Soil	132318	115985
RD-2	Roadside Soil	16086	NA
RD-3	Roadside Soil	28472	NA
RD-4	Roadside Soil	14783	NA
835 Cross	Residential Soil	2639	2653
517 Long	Residential Soil	3087	2530
515 Thurwell	Residential Soil	1240	1317
928 Church	Residential Soil	665	645
306 Main	Residential Soil	3332	3141
552 ~~522~~ Reservoir	Residential Soil	5484	5023
824 Brown	Residential Soil	1112	979
430 Hill	Residential Soil	2457	2425
425 Hill	Residential Soil	2094	2089
511 Long	Residential Soil	1992	1872
300 St Louis	Residential Soil	698	708
351 Short	Residential Soil	940	658

NA= No material > 250 micron was found.

Table 4.3. State Atmospheric Dust Samples.

Filter Number	Location	Flow Rate (m^3/min)
7061239	Bluff	1.37
3018793	Bluff	1.35
6778874	Bluff	1.33
9013631	Bluff	1.33
7061296	Bluff	1.34
3003047	Herky Broad 57	1.43
61011900	Herky Broad 57	1.32
2003046	Herky Broad 57	1.36
9013217	Herky Broad 57	1.26
7061528	Herky Broad 57	1.34

4.03 Precision and Accuracy

The precision of the EMPA speciation will be determined based on sample duplicates run a minimum of every 20 samples. The accuracy of the frequency of occurrence estimates will be determined from a statistical evaluation of point counting data based on the method of Mosimann (1965). These data will be tabulated in Tables 4.4-4.10 as $E^{95\%}$.

4.1 Doe Run Facility Samples

Media from the Doe Run facility were collected from various operational units and ranged in bulk lead concentration from 30488-483095 mg/kg. The baghouse samples have lead masses almost exclusively (84% of the relative lead mass) dominated by galena (PbS), lead salt ($PbKCl_4$) and anglesite+ ($Pb_{1-x}SO_4$-OH) with minor contributions from other lead forms, Figure 4.2, Table 4.4. The particle- size distribution for all lead species is normally distributed with a mean of approximately 35 microns.

There are some differences in major lead forms identified in the various baghouse samples. Baghouse #3 has most of its relative lead mass (82%) dominated by a "lead salt". This lead form is composed of lead (41 wt %) along with potassium, chloride, and sulfate. It generally forms large (272 µ) mats of smaller particles, Photo 1.

Photo 1A. Backscatter image and EDS x-ray spectra of lead salt found in Baghouse #3.

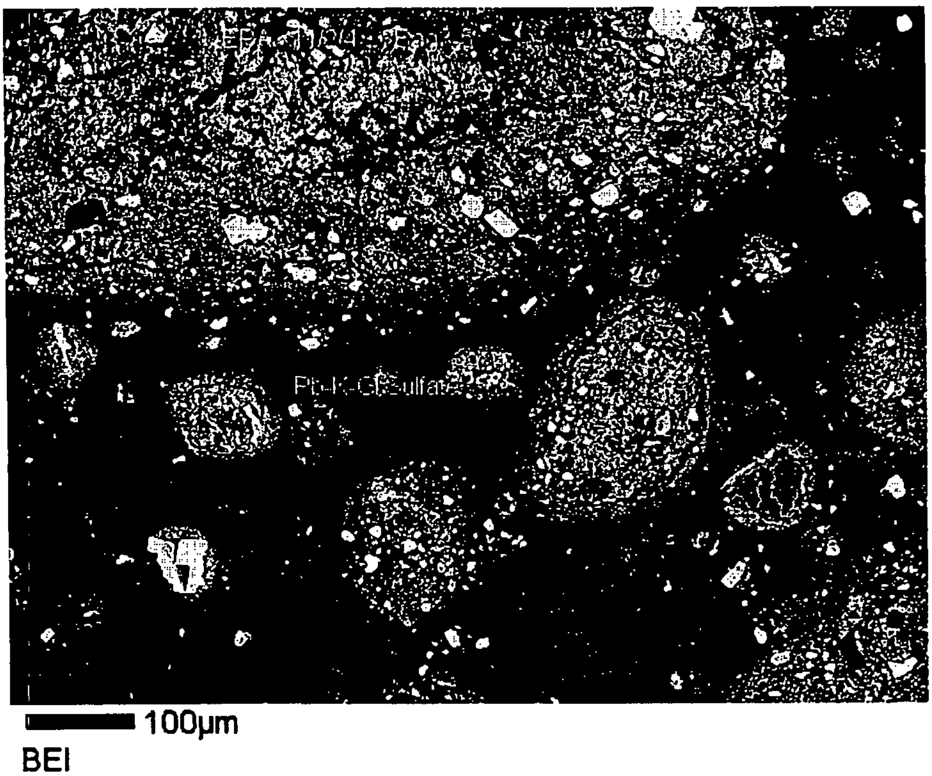
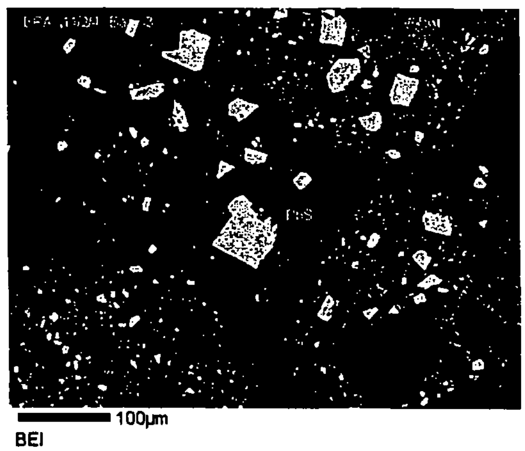
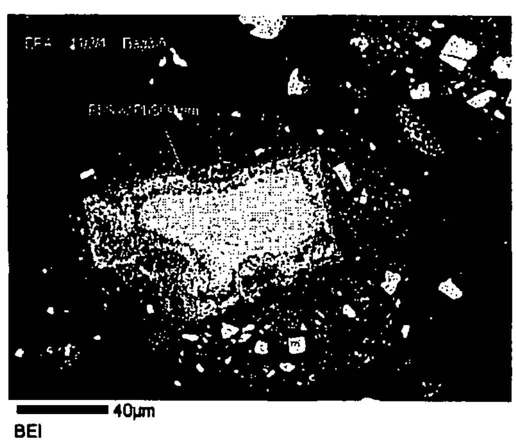


Photo 1B. Characteristic galena, anglesite+, and anglesite particles found in Doe Run baghouse samples



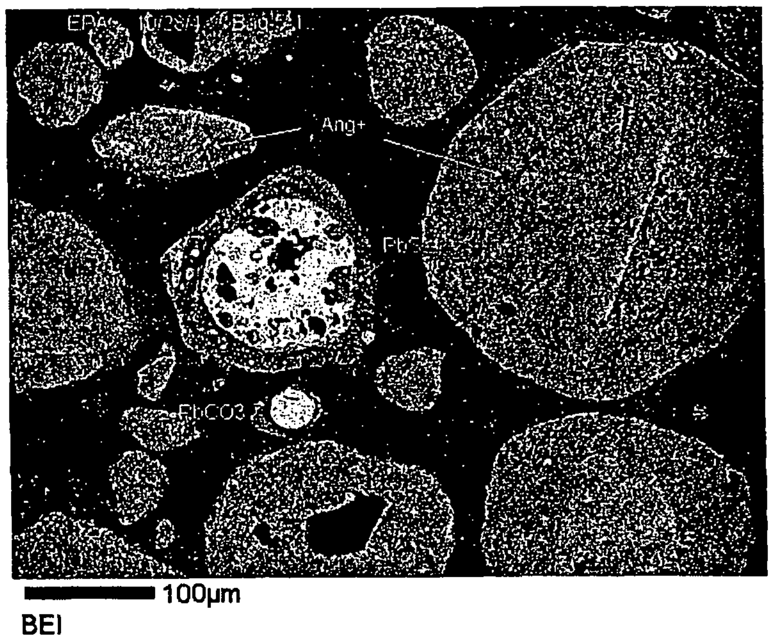


Baghouses # 5 and 6 have similar distributions of relative lead mass, with 76% and 71%, respectively in a phase identified as "anglesite+". This form of lead is a hydrated form of anglesite ($PbSO_4$) a common oxidation product of galena (PbS). Anglesite+ has significantly less lead (38-40 wt%) than anglesite (68 wt%) and may have less sulfur along with traces of other metals. Anglesite+ is generally found in matts averaging approximately 80μ in there longest dimension, but composed of much smaller individual particles, Photo 2.

Baghouse #7 is different from the previous samples in that its relative lead mass is dominated (83%) byy small (4μ) particles of galena (PbS), Photo 3.

Finally, the cooler baghouse is characterized by much coarser particles. With relative lead masses dominated by galena (64%, 23μ) and lead oxide (20%, 27μ), Photo 4.

Photo 2. Backscatter images of anglesite+, found in baghouses 5 and 6.



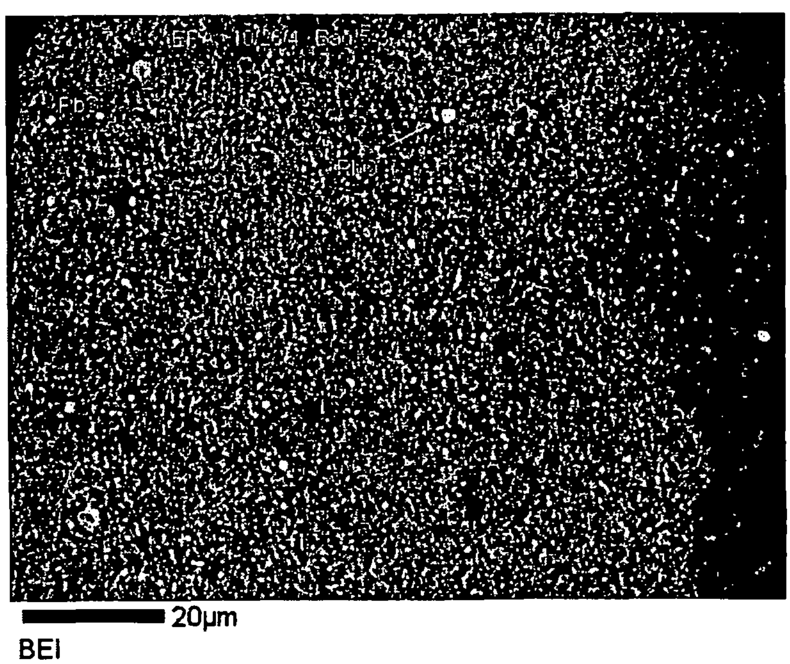
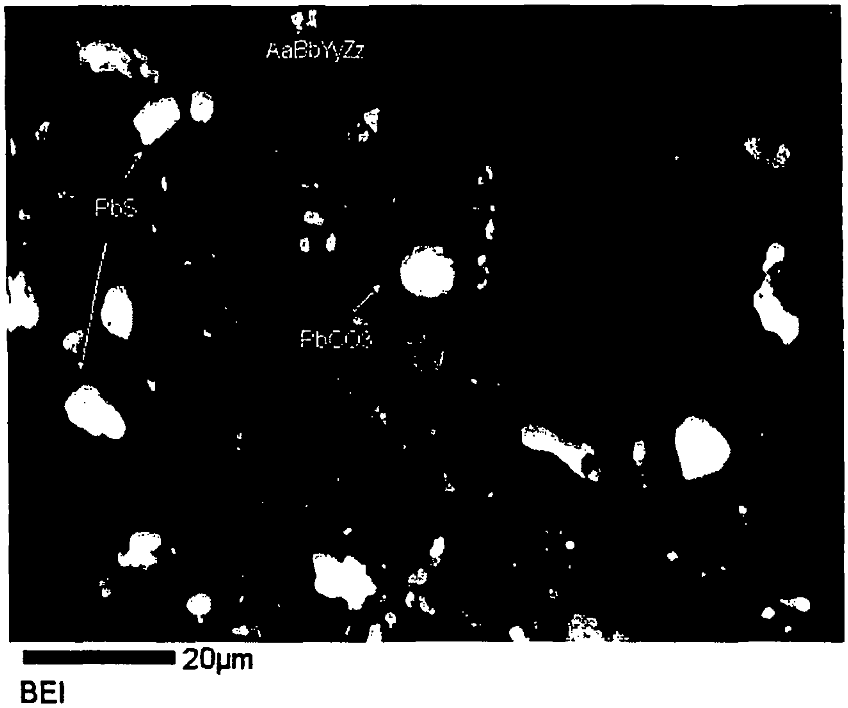


Photo 3. Backscatter images of galena (PbS) particles from baghouse #7.



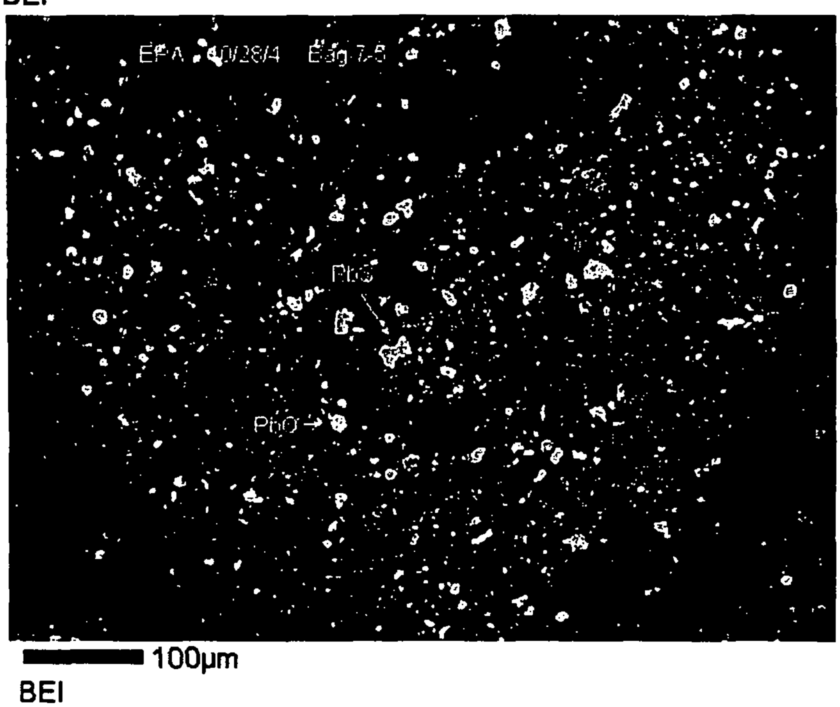


Photo 4. Backscatter image of characteristically large particles of galena and lead oxide from the cooler baghouse sample.

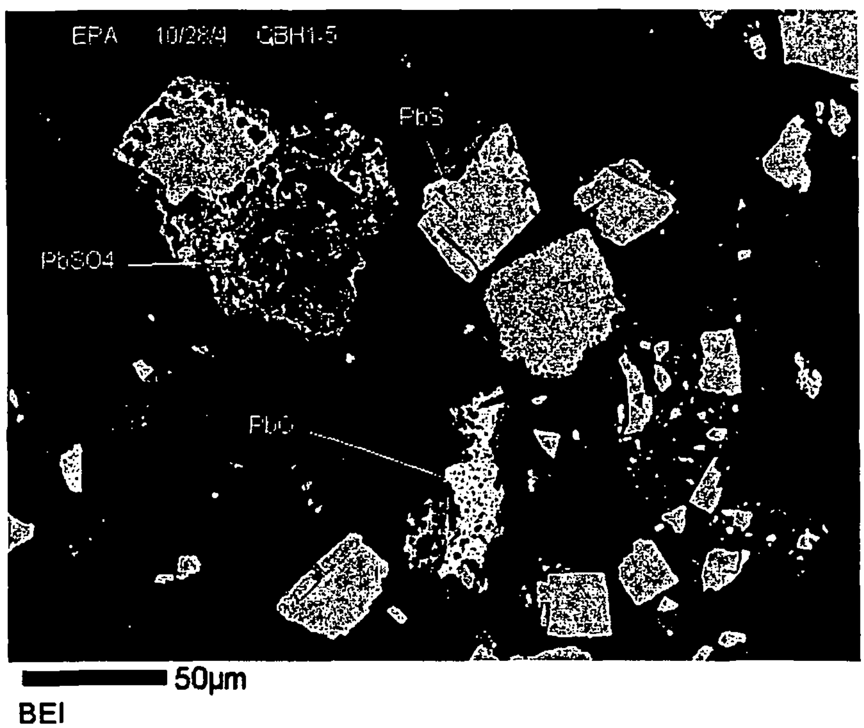


Figure 4.2. Speciation Summary for Baghouses.

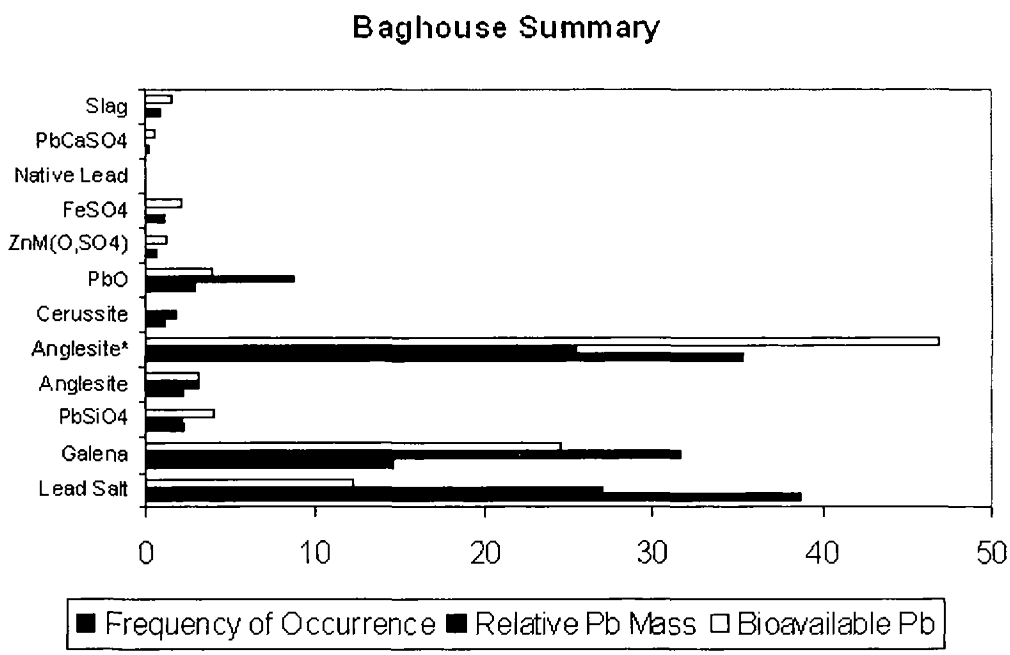


Table 4.4. Speciation for Baghouse Samples.

Sample	Form	F %	F-Bio %	Rm %	BioRm %	Error-95%	Mean Particle Size Microns
Baghouse 3							
	Pb Salt	92.56	68.74	81.5	33.96	2.86	271.92
	Galena	5.63	23.41	15.43	54.65	2.51	5.78
	PbSiO4	0.27	1.17	0.28	1.05	0.57	14.5
	Anglesite	1.54	6.67	2.8	10.33	1.34	8.92
Baghouse 5							
	Anglesite+	90.34	100	76.11	100	4.27	72.78
	Galena	2.76	Tr	6.94	Tr	2.37	5
	Cerussite	2.91	Tr	5.77	Tr	2.43	23
	PbO	2.59	Tr	8.85	Tr	2.29	37.5
	Anglesite	1.4	Tr	2.34	Tr	1.7	11.09
Baghouse 6							
	Anglesite+	88.3	93.95	71.46	84.49	4.07	84.35
	Galena	6.19	5.91	15.3	15.28	3.05	7.98
	Cerussite	2.28	Tr	4.45	Tr	1.89	23
	PbO	2.03	Tr	6.83	Tr	1.78	37.5
	Anglesite	1.19	0.13	1.95	0.23	1.37	6.29
Baghouse 7							
	FeSO4	3.13	3.14	0.16	0.16	1.63	5.56
	Galena	58.08	58.03	83.47	83.44	4.61	4
	Anglesite	4.7	4.71	4.48	4.49	1.98	2.59
	ZnMO/ZnMSO4	18.24	18.26	0.35	0.35	4	4.5
	PbSiO4	1.75	1.76	0.94	0.94	1.23	4.67
	Cerussite	1.69	1.69	1.92	1.92	1.2	6.75
	PbO	3.95	3.95	7.72	7.73	1.82	7
	Native Lead	0.19	0.19	0.47	0.47	0.4	3
	Ca Sulfate	8.27	8.28	0.5	0.5	2.57	2.13
Cooler Baghouse							
	Slag	5.18	5.27	0.05	0.05	2.63	108.25
	FeSO4	6.22	6.33	0.04	0.04	2.87	130
	Galena	52.67	51.84	64.44	63.67	5.93	22.58
	Anglesite+	5.56	5.66	2.39	2.44	2.72	77.5
	PbSiO4	12.25	12.46	8.4	8.58	3.9	64
	Anglesite	5.73	5.83	4.65	4.75	2.76	53.22
	ZnMO/ZnMSO4	0.36	0.37	0.01	0.01	0.71	30
	PbO	12.03	12.24	20.02	20.46	3.87	27.19

F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965. Tr= Trace value.

The term "slag" can have two definitions. One is a very general mineral processing definition used to identify the molten (then cooled) waste product from pyrometalurgical reduction of metal ores. This material contains both a low-lead, "glassy" fraction and high-lead fractions of various oxides, sulfides and sulfates that represent non-smelted or partially smelted phases that did not settled out of the melt prior to removal. The other, more of a mineralogical definition, only refers to the "glassy" portion of a slag-waste sample. It is a Si-Ca-Fe oxide (generally amorphous) and commonly contains only 500-5000 mg/kg lead.

Slag-waste samples have lead masses almost exclusively (87% of the relative lead mass) dominated by native lead (Pb), lead oxide (PbO), anglesite ($PbSO_4$) and galena (PbS) with minor contributions from other lead forms, Figure 4.3, Table 4.5. The particle- size distribution for all lead species is normally distributed with a mean of approximately 85 microns, Photo 5.

Figure 4.3. Speciation Summary for Slag-Waste Samples.

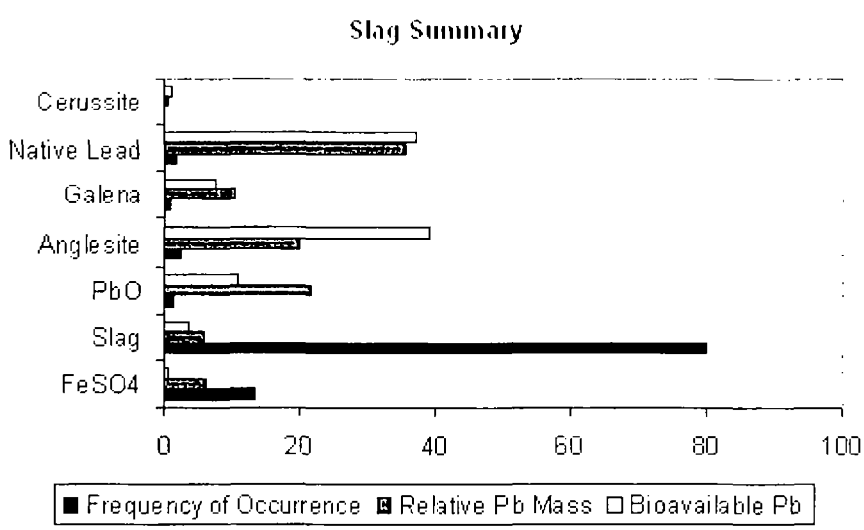
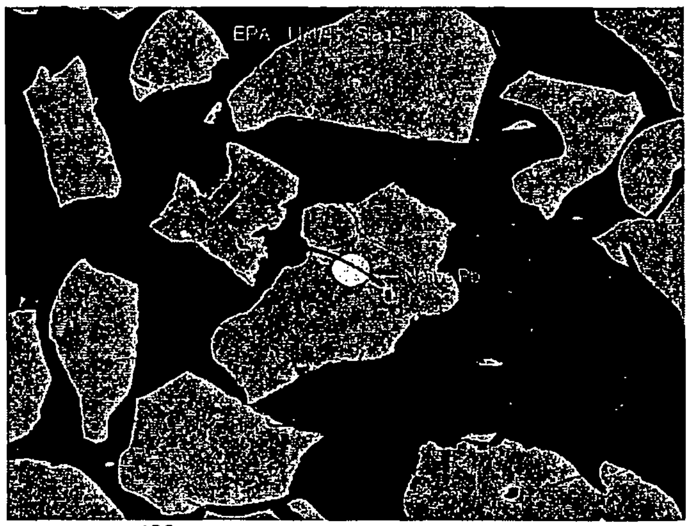


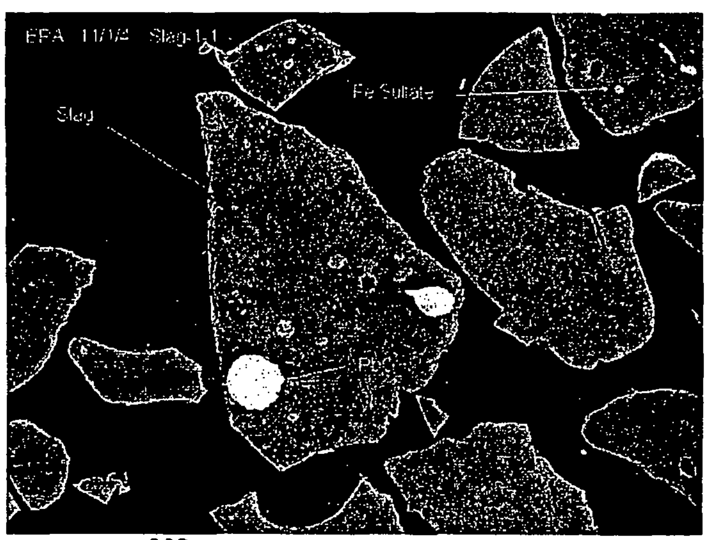
Table 4.5. Speciation of Slag-Waste Samples.

Sample	Form	F %	F-Bio %	Rm %	BioRm %	Error-95%	Mean Particle Size Microns
Slag-1							
	FeSO4	9.01	3.55	4.7	1.88	3.41	19.08
	Slag	84.1	87.22	6.19	7.8	4.36	149.39
	PbO	1.93	0.97	34.51	17.49	1.64	28.91
	Anglesite	3.36	8.27	29.38	72.84	2.15	18.5
	Galena	1.19	Tr	15.64	Tr	1.29	3.7
	Native Lead	0.42	Tr	9.58	Tr	0.77	13.8
Slag-2							
	Slag	77.13	73.78	5.75	1.71	6	307.5
	Native Lead	2.72	9.12	51.44	53.06	2.32	14.8
	FeSO4	16.49	0.33	7.02	0.04	5.31	87.67
	PbO	0.92	1.76	13.58	8.02	1.36	68.33
	Galena	0.64	3.2	6.92	10.7	1.14	5.26
	Anglesite	1.99	11.21	14.38	24.87	2	40.45
	Cerussite	0.11	0.6	0.92	1.59	0.47	3

F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965. Tr = Trace value.

Photo 5. Characteristic particles found in Doe Run slag-waste samples





Concentrate samples have lead masses almost exclusively (98% of the relative lead mass) dominated by galena (PbS) with a minor contribution from cerussite ($PbCO_3$)., Figure 4.4, Table 4.6. The particle- size distribution for all lead species is normally distributed with a mean of approximately 12 microns, Photo 6.

Figure 4.4. Speciation Summary of Concentrate.

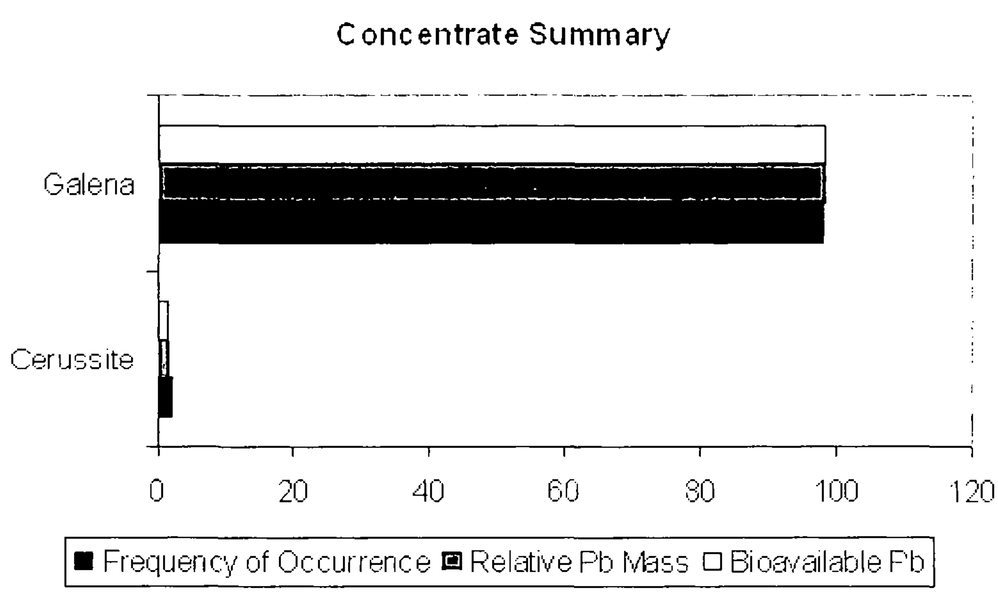
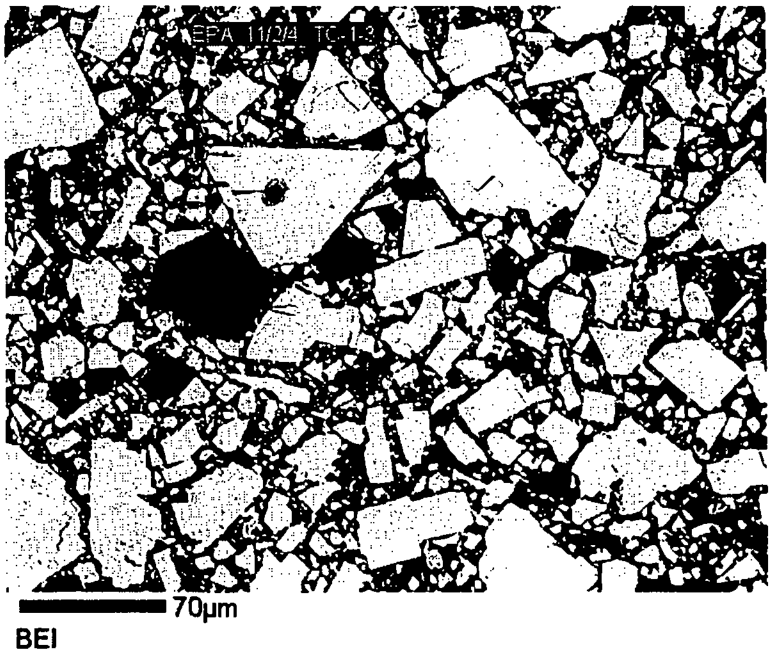


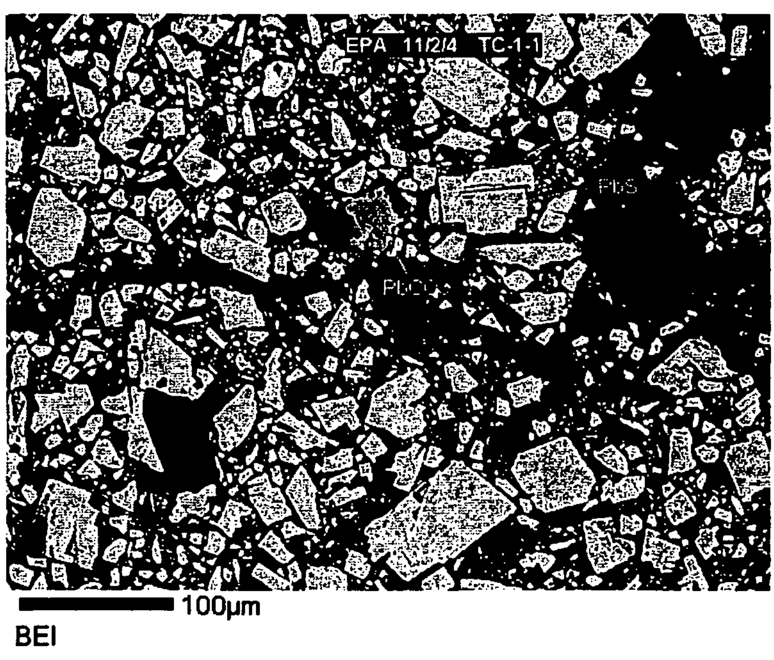
Table 4.6. Speciation of Concentrate.

Sample	Form	F %	F-Bio %	Rm %	BioRm %	Error-95%	Mean Particle Size Microns
Concentrate-1							
	Cerussite	0.37	0.37	0.3	0.3	0.48	32
	Galena	99.63	99.63	99.7	99.7	0.48	13.53
Concentrate-2							
	Cerussite	3.73	3.73	2.97	2.97	1.31	10.79
	Galena	96.27	96.27	97.03	97.03	1.31	9.99

F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965.

Photo 6. Characteristic galena particles found in Doe Run concentrate samples.



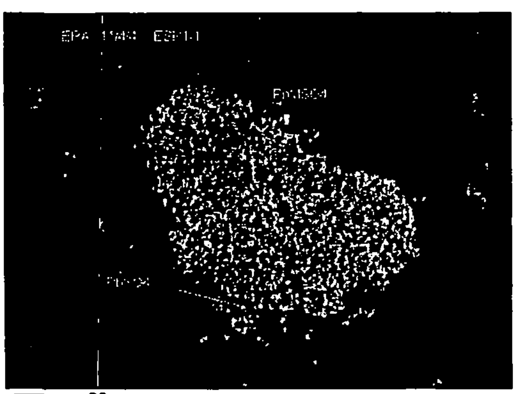


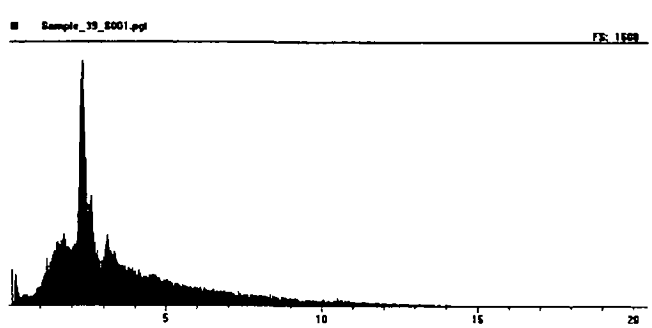
A sample from the electrostatic precipitator has 99% of the relative lead mass associated with lead-metal sulfate ($PbMSO_4$) that may or may not contain chlorine and galena (PbS), Table 4.7 averaging 78 and 10 microns in size, respectively, Photo 7.

Table 4.7. Electro Static Precipitator Sample.

Sample	Form	F %	F-Bio %	Rm %	BioRm %	Error-95%	Mean Particle Size Microns
ElectroStatic Precipitator	PbMSO4	99.96	99.59	89.94	98.15	2.15	77.94
	Galena	0.04	0.41	10.01	1.85	2.15	9.77
	Anglesite	Tr	Tr	0.04	Tr	0.18	1

Photo 7. Backscatter and EDS spectra of $PbMSO_4$ from electro Static Precipitator.


20µm
BEI



4.2 Roadside Samples

Bulk lead concentrations from the four roadside samples collected during this investigation range from 16085-132318 mg/kg.. These samples have lead masses almost exclusively (90% of the relative lead mass) dominated by galena (PbS), cerussite ($PbCO_3$) and anglesite ($PbSO_4$) with minor contributions from other lead forms, Figure 4.5, Table 4.8. The particle- size distribution for all lead species is normally distributed with a mean of approximately 20 microns, Photo 8 . The roadside samples contain source-traceable lead forms providing good evidence that facility activity contributed to the elevated lead concentrations.

Figure 4.5. Speciation Summary of Roadside Soils.

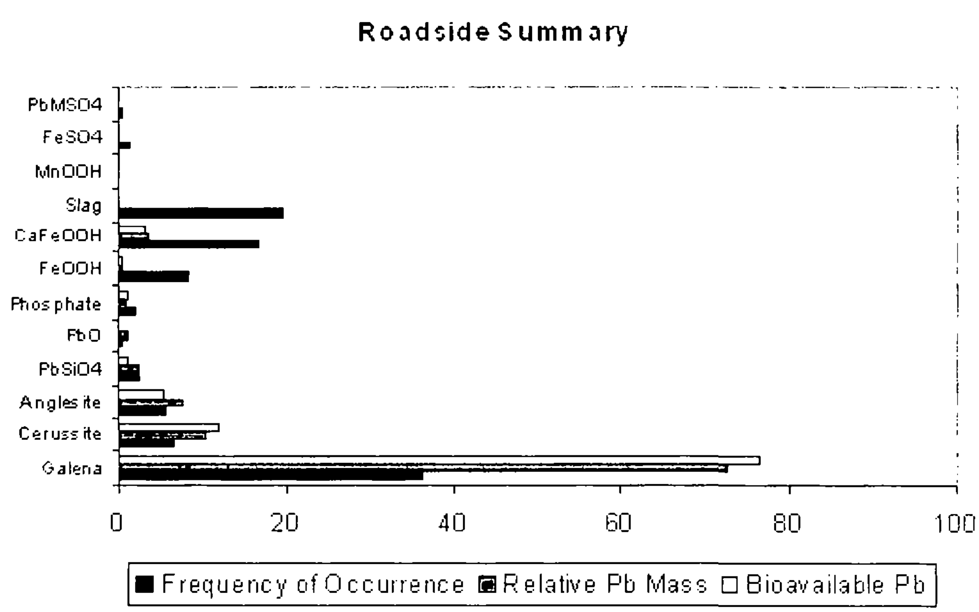
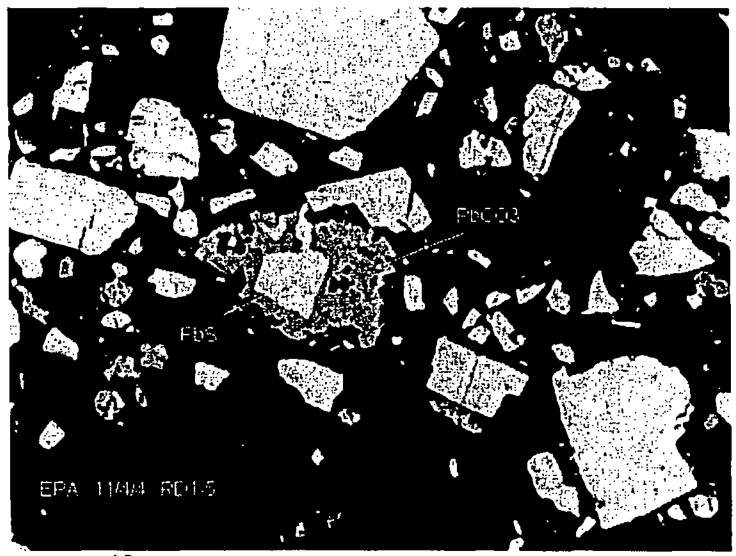


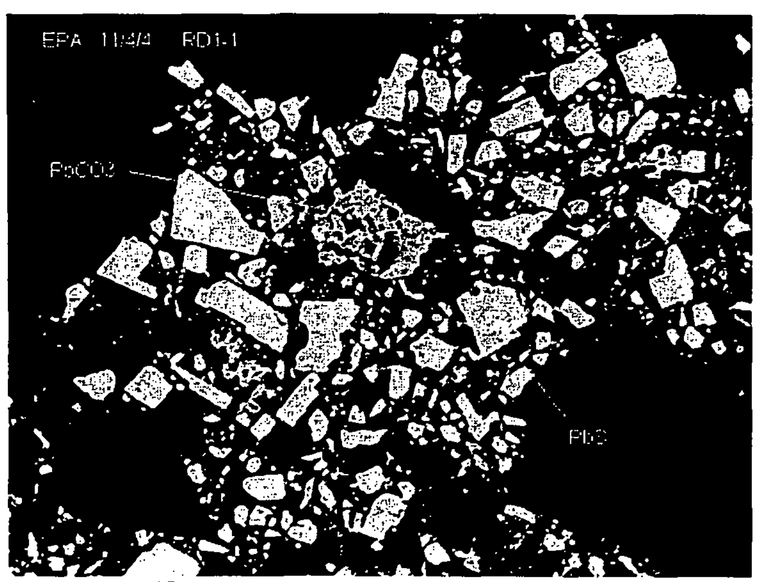
Table 4.8. Speciation of Roadside Soils.

Sample	Form	F %	F-Bio %	Rm %	BioRm %	Error-95%	Mean Particle Size Microns
Road-1							
	Galena	74.78	85.97	79.44	88.78	4.7	11.29
	Cerussite	11.17	12.86	9.35	10.48	3.41	4.63
	Anglesite	11.22	Tr	7.91	Tr	3.42	400
	PbSiO4	1.01	1.16	0.66	0.74	1.08	36
	PbO	1.82	Tr	2.64	Tr	1.45	16.25
Road-2							
	Phosphate	4.26	8.77	2.27	5.91	3.01	28
	Anglesite	6.79	13.97	10.82	28.11	3.75	15.93
	Galena	9.66	12.56	23.22	38.09	4.4	13.23
	FeOOH	8.31	17.1	0.55	1.44	4.11	34.13
	CaFeO	21.01	19.61	5.69	6.65	6.07	30.02
	Cerussite	25.67	6.48	48.64	15.51	6.51	129.77
	Slag	18.26	18.79	0.34	0.44	5.76	150
	PbSiO4	5.72	2.07	8.47	3.86	3.46	125.33
	MnOOH	0.32	0.66	Tr	Tr	0.84	21
Road-3							
	CaFeO	31.22	34.16	9	9.02	5.74	26.36
	Phosphate	1.96	2.14	1.18	1.18	1.72	16
	FeOOH	7.82	8.56	0.57	0.57	3.33	31.92
	Galena	31.98	34.96	83.82	83.96	5.78	10.3
	Cerussite	0.71	0.78	1.48	1.48	1.04	11.67
	FeSO4	0.39	0.42	0.04	0.04	0.77	9.5
	Anglesite	0.61	0.67	1.07	1.07	0.97	7.5
	PbSiO4	1.23	1.34	1.98	1.98	1.36	20
	Slag	22.65	15.39	0.42	0.25	5.19	123.22
	PbMSO4	1.43	1.56	0.44	0.44	1.47	70
Road-4							
	Galena	27.65	49.08	75.02	74.24	8.04	20.87
	Anglesite	2.69	5.6	4.83	5.63	2.9	6.91
	CaFeO	1.43	2.99	0.44	0.51	2.13	40.5
	Cerussite	7.75	16.19	16.59	19.31	4.81	48.78
	Slag	20.63	13.75	0.43	0.16	7.27	233.6
	FeOOH	36.04	4.42	2.68	0.15	8.63	510
	MnOOH	0.28	0.59	Tr	Tr	0.95	16
	FeSO4	3.53	7.37	Tr	Tr	3.32	200

F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965. Tr= trace value.

Photo 8. Characteristic galena and cerussite particles found in Herculaneum roadside samples.





4.3 Residential Interior Dusts

Ten residential dust samples were collected with bulk lead concentrations between 1272-24651 mg/kg. These samples have lead masses almost exclusively (91% of the relative lead mass) dominated by galena (PbS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$) with minor contributions from other lead forms, Figure 4.6, Table 4.9. The particle- size distribution for all lead species is normally distributed with a mean of approximately 5 microns, Photos 5-6 . The dust samples contain source-traceable lead forms ($PbCl_4$, $PbMSO_4$, PbMO, Slag, and Galena) providing good evidence that facility activity (emissions, hauling, storage) contributed to the elevated lead concentrations.

Figure 4.6. Summary of Dust Speciation Results.

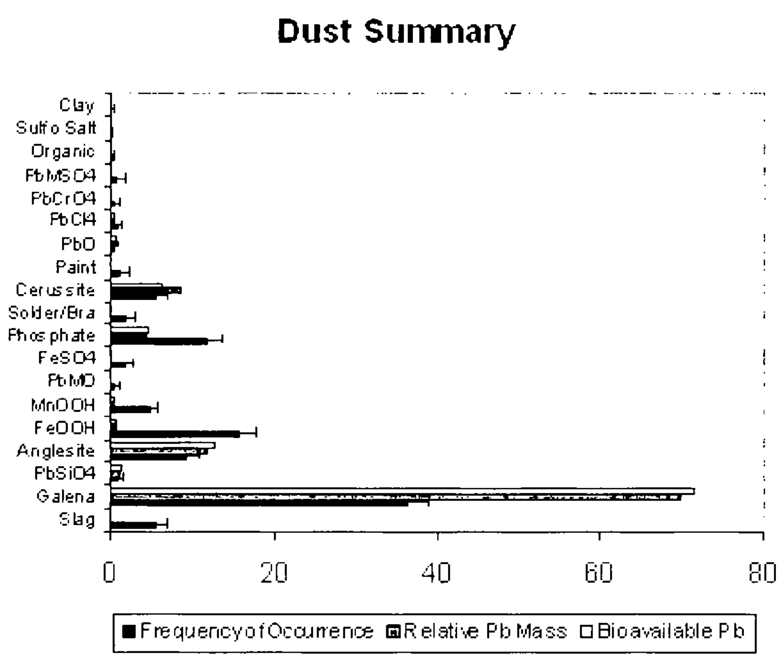


Table 4.9. Interior Dust Speciation.

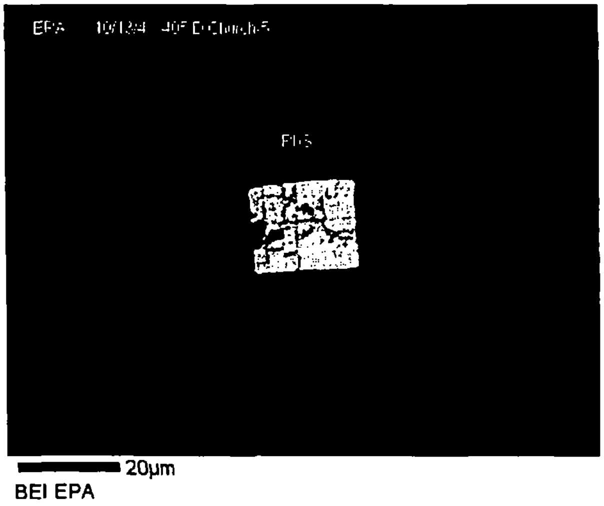
Sample	Form	F	F-Bio	Rm	BioRm	Error-95%	Mean Particle Size
		%	%	%	%		Microns
306 Main							
	Anglesite	10.74	10.87	11.45	11.63	6.04	1.75
	Cerussite	4.91	3.73	6.22	4.74	4.21	3.2
	Galena	48.47	49.07	77.89	79.12	9.75	2.87
	Phosphate	8.59	8.7	2.15	2.18	5.46	7
	FeOOH	12.58	12.73	0.52	0.53	6.47	4.1
	PbCl4	0.61	0.62	0.66	0.67	1.52	2
	PbMSO4	0.92	0.93	0.17	0.18	1.86	3
	MnOOH	5.21	5.28	0.92	0.93	4.34	5.67
	Brass	7.98	8.07	0.03	0.03	5.28	13
320 Curved							
	Galena	22.27	21.86	59.93	59.43	7.24	2.73
	Cerussite	3.32	3.39	7.04	7.26	3.12	8
	PbSiO4	1.11	1.13	1.83	1.89	1.82	4
	Anglesite	3.46	3.53	6.17	6.36	3.18	5
	PbCaO	2.77	2.82	Tr	Tr	2.85	20
	Phosphate	43.15	42.88	23.06	23.05	8.61	8.43
	FeOOH	4.15	4.23	0.23	0.23	3.47	7.5
	MnOOH	5.53	5.64	1.63	1.68	3.98	4
	PbMSO4	3.73	3.81	Tr	Tr	3.3	27
	Slag	3.46	3.53	Tr	Tr	3.18	25
	Lead Solder	0.14	0.14	0.03	0.03	0.65	1
	PbCl4	5.95	6.06	Tr	Tr	4.11	43
	FeSO4	0.55	0.56	Tr	Tr	1.29	4
	BiMO	0.41	0.42	0.08	0.08	1.12	3
? 405 Church							
	Galena	38.16	38.2	71.07	71.17	8.05	5.9
	Cerussite	7.63	7.54	11.21	11.08	4.4	4.94
	Organic	2.42	2.42	0.05	0.05	2.54	25
	FeSO4	4.54	4.55	0.34	0.34	3.45	15.67
	Anglesite	8.41	8.41	10.39	10.4	4.6	4.58
	Slag	11.01	11.03	0.16	0.16	5.19	38
	Phosphate	14.49	14.51	5.78	5.79	5.83	8.82
	CuMSO4	0.58	0.58	0.09	0.09	1.26	6
	MnOOH	6.28	6.29	0.59	0.59	4.02	21.67
	FeOOH	6.47	6.48	0.33	0.33	4.08	6.7
430 Hill							
	FeOOH	64.02	64.02	13.53	13.53	9.27	13.12
	Phosphate	1.02	1.02	1.79	1.79	1.94	4.5
	Cerussite	1.93	1.93	11.61	11.61	2.66	8.5
	Galena	8.29	8.29	63.2	63.2	5.32	2.43
	FeSO4	2.38	2.38	0.41	0.41	2.95	10.5
	ZnMSO4	1.36	1.36	0.13	0.13	2.24	2.4
	Anglesite	0.45	0.45	2.3	2.3	1.3	2
	MnOOH	12.03	12.03	5.3	5.3	6.28	13.25
	Clay	1.7	1.7	0.12	0.12	2.5	3
	Paint?	2.84	2.84	0.9	0.9	3.21	12.5
	Sulfo Salt	0.34	0.34	0.5	0.5	1.13	3
	Slag	3.63	3.63	0.21	0.21	3.61	32

Sample	Form	F	F-Bio	Rm	BioRm	error-95%	Mean Particle Size
		%	%	%	%		Microns
511 Long							
	FeOOH	13.78	14.52	0.58	0.62	6.02	6.75
	Galena	46.6	45.16	74.49	73.54	8.71	3.51
	Paint	4.93	5.2	0.33	0.35	3.78	29
	FeSO4	5.27	4.84	0.29	0.31	3.9	5.17
	Cerussite	8.5	8.24	10.72	10.58	4.87	5
	Anglesite	10.71	11.29	11.36	12.2	5.4	5.73
	PbCl4	0.34	0.36	0.37	0.39	1.02	2
	MnOOH	0.68	0.72	0.12	0.13	1.44	4
	Slag	4.76	5.02	0.04	0.04	3.72	14
	Phosphate	3.57	3.76	0.87	0.94	3.24	7
	PbSiO4	0.85	0.9	0.84	0.9	1.6	5
515 Thurwell							
	FeOOH	18.45	18.54	0.91	0.91	7.03	8.23
	PbCl4	1.55	1.56	1.33	1.33	2.24	1.29
	Galena	37.76	37.95	72.33	72.38	8.78	4.76
	Cerussite	9.31	9.36	14.06	14.07	5.27	2.84
	Phosphate	5.52	5.55	1.29	1.29	4.14	6.4
	Lead Solder	5.69	5.2	0.61	0.54	4.2	3.3
	MnOOH	5.34	5.37	0.72	0.72	4.08	6.2
	PbMO	0.34	0.35	Tr	Tr	1.06	2
	Anglesite	3.79	3.81	4.82	4.82	3.46	3.14
	PbSiO4	2.93	2.95	3.46	3.46	3.06	17
	PbCaO	1.55	1.56	0.47	0.47	2.24	4.5
	PbSnCl	7.76	7.8	Tr	Tr	4.85	45
552 Reservoir							
	Slag	16.82	17.02	0.24	0.24	9.88	14
	Galena	23.42	23.71	66.39	67.44	11.19	3.55
	PbSiO4	8.41	8.51	14.68	14.91	7.33	14
	Anglesite	6.31	6.08	11.86	11.47	6.42	3
	FeOOH	22.22	22.49	1.75	1.77	10.99	10.57
	MnOOH	6.61	6.69	2.05	2.08	6.56	22
	Brass	3.3	3.34	0.01	0.01	4.72	5.5
	ZnMSO4	2.4	2.43	0.08	0.09	4.05	8
	PbMO	0.9	Tr	0.98	Tr	2.5	1
	FeSO4	3	3.04	0.34	0.34	4.51	10
	ZnMO	3.6	3.65	Tr	Tr	4.93	12
	Phosphate	2.7	2.74	1.56	1.59	4.29	3
	Lead Solder	0.3	0.3	0.06	0.06	1.45	1
774 Circle							
	Cerussite	3.4	2.99	4.76	4.36	2.78	4.78
	Clay	0.24	0.25	Tr	Tr	0.75	3
	Slag	3.4	3.57	0.05	0.05	2.78	10.75
	Phosphate	20.74	21.78	6.93	7.58	6.21	9.03
	MnOOH	5.23	5.49	0.8	0.87	3.41	16.5
	ZnMO	0.95	1	0.02	0.02	1.48	12
	Galena	37.45	35.41	66.46	65.44	7.41	5.63
	FeOOH	12.59	13.22	0.61	0.66	5.08	15.9
	FeSO4	0.63	0.67	Tr	Tr	1.21	8
	PbO	2.22	1.83	5.35	4.6	2.25	14
	Anglesite	12.19	12.8	14.36	15.7	5.01	9.63
	Lead Solder	0.4	0.42	0.05	0.05	0.96	2.5
	PbSiO4	0.55	0.58	0.61	0.66	1.14	7

Sample	Form	F	F-Bio	Rm	BioRm	error-95%	Mean Particle Size
		%	%	%	%		Microns
785 Circle							
	Phosphate	7.9	9.64	2.56	3.3	4.5	1.83
	Galena	36.36	43.64	57.83	73.53	8.03	4.07
	Anglesite	11.62	14.18	12.27	15.86	5.35	4.59
	Lead Solder	1.19	1.45	0.13	0.17	1.81	8
	Brass	0.45	0.55	0.01	0.01	1.11	3
	Slag	4.32	5.27	0.04	0.05	3.39	9.67
	FeSO4	1.79	2	0.11	0.13	2.21	4
	Paint	6.71	8.18	0.44	0.57	4.17	45
	Cerussite	18.78	1.82	23.55	2.42	6.52	18
	FeOOH	1.49	1.82	0.07	0.08	2.02	5
	ZnMO	1.94	2.36	Tr	Tr	2.3	13
	PbCRO4	1.79	2.18	1.26	1.63	2.21	12
	CrMO	2.83	3.45	0.05	0.07	2.77	2.71
	PbSiO4	0.89	1.09	0.88	1.13	1.57	6
	PbMSO4	0.89	1.09	0.17	0.22	1.57	2
	PbMO	1.04	1.27	0.64	0.83	1.7	7
835 Cross							
	Galena	63.4	62.81	78.74	78.32	7.9	6.46
	FeSO4	0.95	0.96	0.05	0.05	1.59	4.5
	Anglesite	20.89	21.22	17.21	17.56	6.66	5.5
	PbCl4	1.79	1.82	1.5	1.53	2.18	8.5
	Cerussite	1.48	1.5	1.45	1.48	1.98	7
	Slag	8.86	9	0.04	0.04	4.66	21
	FeOOH	1.37	1.39	0.05	0.05	1.91	6.5
	PbSiO4	1.27	1.29	0.97	0.99	1.83	6

F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965. Tr = trace value.

Photo 5. Characteristic galena particles found in Herculaneum dust samples.



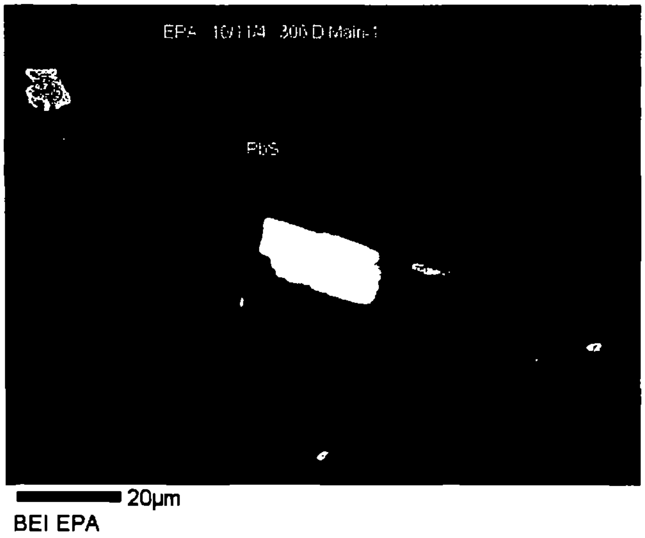
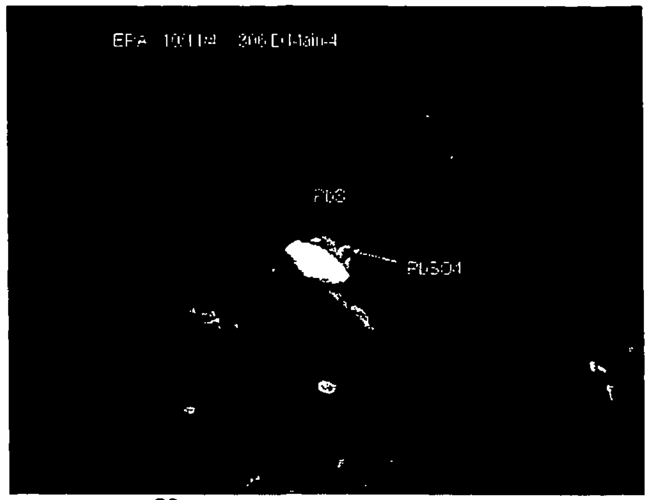
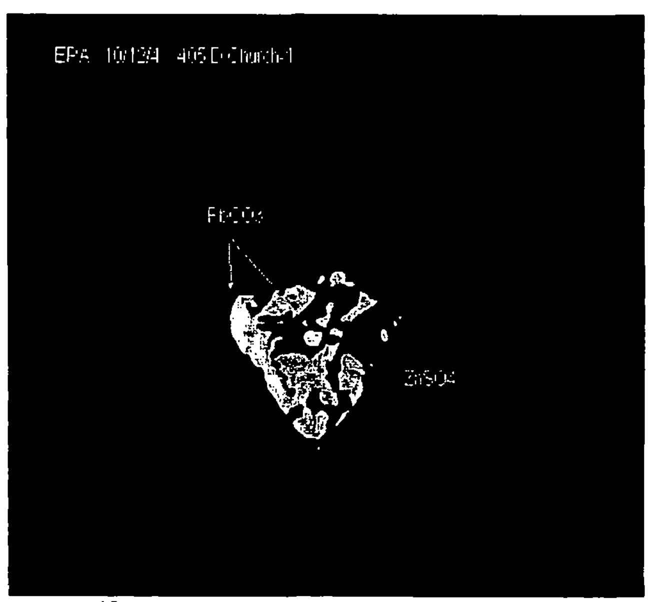


Photo 6. Characteristic cerussite and galena particles from Herculaneum dust.



20µm
BEI EPA



10µm
BEI EPA

4.4 Residential Soils

The residential soil sample set (Figure 1) includes soils with varied bulk lead concentrations (658-5023 mg/kg). These samples have lead masses (74% of the relative lead mass) dominated by MnOOH, $PbCO_3$, phosphates, and PbS, with minor contributions from other lead forms, Figure 4.7, Table 4.10. The MnOOH and $PbCO_3$ particles are larger, and generally cemented or liberated, Photo 7 with a median particle size of 13 microns, while the PbS and phosphate particles are generally finer at 4 microns, Photo 8.

The residential soils contain source-traceable lead forms (slag, PbMO, PbMSO4, galena) similar to those observed in dust samples, Table 4.9; however, the "soil interacting" forms: Mn oxide, Fe oxide and phosphate are more prevalent as is typical in developed soil environments. These forms are the result of soluble lead sorbing onto Mn, Fe, and/or P minerals that are found in soils. No lead-bearing paint particles were found in the residential soil samples. Further, of the traceable lead forms: native lead, $PbSiO_4$ and PbS are not used as pigments, and only PbO, $PbCO_3$, and $PbSO_4$ are known to be lead pigments; however, they are also common to the Doe Run facility. Therefore paint is unlikely to be a major source to the residential-yard lead.

Speciation analyses in itself can not rule out leaded gasoline as a possible lead source, the forms of lead emitted from these historic fuels are generally very soluble and would have released their lead to be sorbed onto the "soil interacting" forms described above. A number of factors however suggest that this is unlikely to be a significant lead source to the overall community; 1) numerous studies (Ward, et al., 1977, Kingston et al., 1988, Solomon and Hartford, 1976, Burguera et al., 1988, and Garcia-Miragaya, 1984,) have shown that soil-lead concentrations from gasoline diminish rapidly to background levels within a few (5-20) meters distance from a major road.

Some studies have further shown that unless traffic volumes are large (>5000 vehicles/day) lead concentrations above background are not found (Burguera et al., 1988) 2) traceable forms of lead that are found in residential soils are related to the Doe Run facility. 3) residential lead concentrations are significantly greater than similar-size communities that have no mining/milling/smelting activities. In conjunction with the speciation work lead isotopic studies could be used to further evaluate a leaded-gasoline source.

Figure 4.7. Residential Soil Speciation Summary.

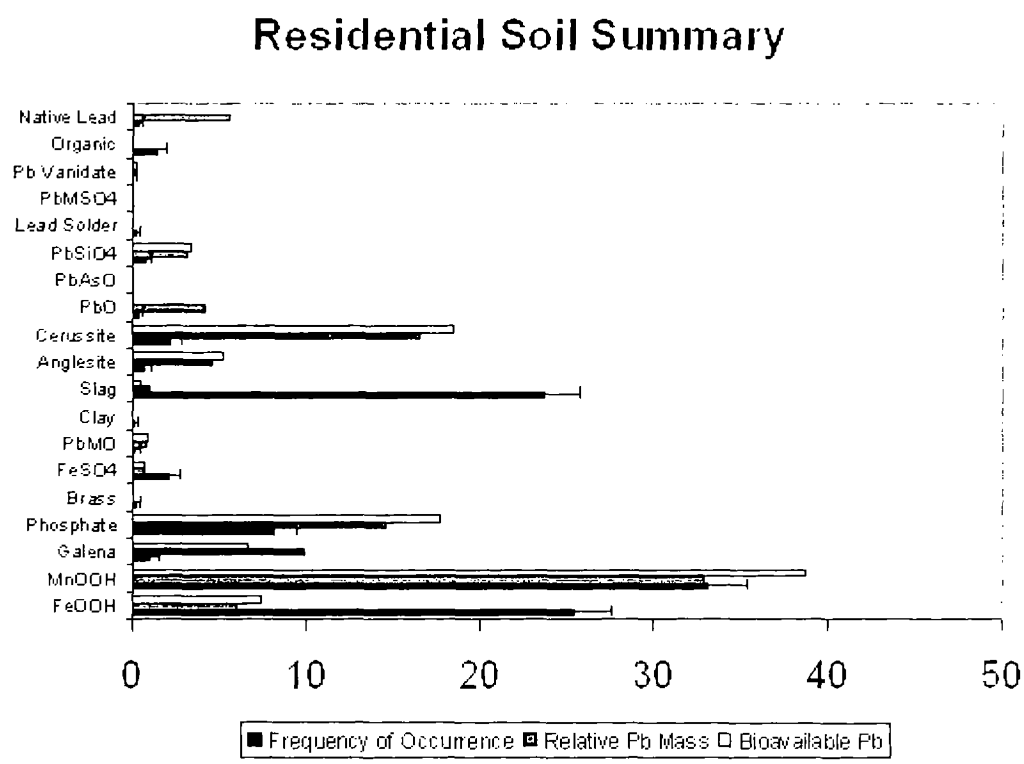


Table 4.10. Residential Soil Speciation.

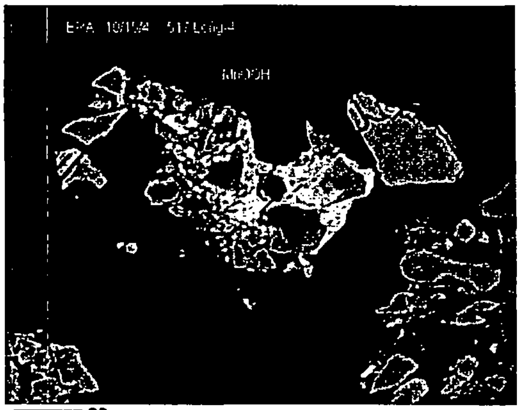
Sample	Form	F %	F-Bio %	Rm %	BioRm %	Error-95%	Mean Particle Size Microns
300 St Louis							
	FeOOH	11.71	65.9	24.77	26.22	9.75	13.27
	Anglesite	Tr	Tr	4.27	Tr	1.06	4
	Cerussite	Tr	Tr	1.27	Tr	0.53	1
	Slag	87.64	Tr	0	Tr	8.03	290
	MnOOH	0.65	32.66	54.22	57.4	8.5	7.95
	Galena	Tr	0.76	12.88	13.64	1.5	8
	Phosphate	Tr	0.67	2.59	2.74	1.4	3.5
306 Main							
	FeOOH	0.2	30.84	9.18	9.25	5.89	22.17
	MnOOH	0.17	48.29	67.31	67.76	6.83	8.5
	Slag	99.6	10.96	0.71	0.71	7.24	272.25
	FeSO4	Tr	3.07	2.27	1.61	2.73	2.71
	Phosphate	0.03	6.84	20.53	20.67	3.03	7.38
351Short							
	Phosphate	78.18	49.56	65.18	64.91	8.84	3.48
	MnOOH	7.61	38.37	26.04	26.25	8.59	6.17
	FeOOH	14.07	10.66	1.86	1.87	5.44	12
	Anglesite	Tr	0.18	0.74	0.75	0.74	1
	Cerussite	0.14	1.24	6.17	6.22	1.95	7
425 Hill							
	Phosphate	8.56	14.1	11.95	11.96	5.94	17.8
	FeOOH	9.38	28.84	9.03	9.03	7.85	19.5
	MnOOH	14.99	55.04	77.47	77.52	9.02	15.55
	Cerussite	Tr	0.11	1.16	1.16	0.55	1
	FeSO4	Tr	0.79	0.29	0.23	1.6	5.67
	Slag	67.05	Tr	Tr	Tr	5.88	260
	Lead Solder	Tr	0.37	Tr	Tr	1.03	7
	Clay	0.01	0.74	0.1	0.1	1.45	14
430 Hill							
	MnOOH	31.99	85.76	51.31	81.27	7.86	21.22
	FeOOH	1.26	8.87	1.51	2.39	4.63	11.35
	Phosphate	0.04	3.81	3.76	5.96	3.11	8.3
	Organic	66.6	Tr	Tr	Tr	5.84	325
	Lead Solder	Tr	0.18	0.08	0.13	0.69	4
	Galena	0.01	0.87	5.37	8.5	1.51	19
	Native Lead	0.09	Tr	36.87	Tr	2.96	15
	NbTiPbO	Tr	0.51	1.11	1.75	1.15	11
511 Long							
	Phosphate	0.09	11.11	Tr	Tr	4.98	6.35
	MnOOH	0.05	20.27	Tr	Tr	6.48	5.63
	FeOOH	3.95	51.13	Tr	Tr	8.86	17.14
	FeSO4	0.05	6.07	Tr	Tr	3.75	14.75
	Slag	95.64	3.29	0.33	0.52	8.27	191
	Anglesite	Tr	0.82	7.15	11.24	1.41	8
	Cerussite	Tr	1.03	10.62	16.69	1.57	10
	Galena	Tr	0.62	44.45	12.7	2.84	1.43
	PbSiO4	0.2	4.63	37.33	58.67	3.3	45
	Brass	Tr	1.03	0.11	0.18	1.57	10

Sample	Form	F	F-Bio	Rm	BioRm	Error-95%	Mean Particle Size
		%	%	%	%		Microns
515 Thurwell							
	Slag	56.91	31.01	2.95	3.01	9.03	57.88
	Anglesite	Tr	Tr	0.78	Tr	0.51	1
	FeSO4	7.3	6.23	5.16	3.97	5.15	4.23
	MnOOH	10.89	24.92	42.69	43.59	8.15	14.43
	Phosphate	0.1	8.86	30.5	31.13	5.32	4.54
	FeOOH	24.78	26.65	9.13	9.32	8.34	27.31
	PbVO	0.02	1.73	5.94	6.06	2.43	5.75
	Galena	Tr	0.15	2.35	2.4	0.72	1
	Lead Solder	Tr	0.45	0.5	0.51	1.25	6
517 Long							
	MnOOH	0.01	10.96	6.68	8.86	3.31	20.83
	Phosphate	Tr	14.37	25.78	32.8	3.83	3.35
	FeOOH	0.15	41.54	7.83	10.39	5.96	18.96
	Lead Solder	Tr	3.16	0.47	0.62	1.81	12
	Slag	99.84	20.6	7.35	0.59	7.51	177.78
	PbSiO4	Tr	5.78	34.8	35.44	2.97	5.88
	pbmso4	Tr	0.26	0.23	0.31	0.52	3
	FeSO4	Tr	2.28	1.36	0.9	2.43	1.94
	Galena	Tr	0.88	14.46	8.72	1.42	1.57
	Cerussite	Tr	0.18	1.04	1.37	0.43	2
552 Reservoir							
	MnOOH	8.15	27.51	17.94	22.51	5.66	30.83
	FeOOH	7.11	38.43	6.63	8.28	6.28	19.9
	Phosphate	0.73	7.54	9.91	12.21	3.3	6.38
	PbAsO	Tr	0.06	0.21	0.26	0.31	2
	Slag	83.81	14.49	1.21	0.69	5.72	131.57
	FeSO4	0.02	2.18	0.54	0.68	1.81	7.89
	Anglesite	0.12	4.31	18.34	22.37	2.55	16
	PbSiO4	0.01	0.58	2.25	2.82	0.94	19
	Cerussite	0.05	4.89	30.12	30.19	2.97	9.95
	Galena	Tr	Tr	12.86	Tr	1.75	1.81
824 Brown							
	FeOOH	1.3	11.72	0.82	0.98	5.84	10.3
	Phosphate	0.1	13.54	7.45	8.87	6.22	3.13
	Galena	0.93	7.85	19.83	23.62	4.88	6.9
	MnOOH	2.37	24.23	6.44	7.67	7.81	6.09
	Anglesite	Tr	0.11	0.19	0.23	0.61	1
	Cerussite	15.82	23.32	46.46	55.33	7.71	25.63
	FeSO4	0.01	1.14	0.11	0.14	1.92	5
	Slag	77.3	15.36	Tr	Tr	6.55	135
	PbMO	0.03	2.73	2.66	3.17	2.95	4
	PbO	2.17	Tr	16.03	Tr	3.82	41
835 Cross							
	MnOOH	81.6	41.32	39.65	39.21	7.97	14.71
	FeSO4	Tr	0.82	0.1	0.14	1.32	5
	FeOOH	9.63	24.17	4.07	5.66	6.43	22.2
	Phosphate	1.2	14.92	21.4	29.77	5.29	7.41
	PbMO	Tr	0.11	0.94	0.37	0.9	2.33
	Clay	0.02	0.98	0.06	0.08	1.44	18
	Slag	7.08	12.14	0.6	0.83	4.84	74.33
	Brass	0.05	2.18	0.12	0.16	2.14	20
	Anglesite	Tr	Tr	0.7	Tr	0.59	3
	Cerussite	0.4	3.38	17.63	23.76	2.69	21.33
	PbO	0.03	Tr	14.73	Tr	1.89	5.17

Sample	Form	F	F-Bio	Rm	BioRm	Error-95%	Mean Particle Size
		%	%	%	%		Microns
928 Church							
	FeOOH	93.9	56.38	13.85	13.85	9.62	26.91
	MnOOH	6.08	35.25	53.22	53.22	9.27	7.44
	Galena	Tr	1.18	16.57	16.57	2.1	4.33
	Phosphate	0.01	4.01	11.99	11.99	3.81	2.93
	Brass	Tr	0.09	0.01	0.01	0.59	1
	FeSO4	0.01	2.55	1.42	1.42	3.06	4.67
	PbMO	Tr	0.55	2.95	2.95	1.43	3

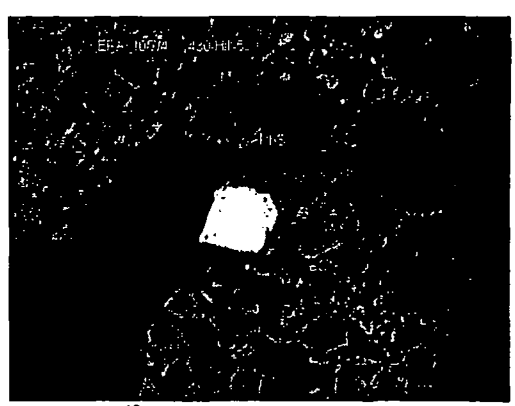
F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965. Tr = trace value.

Photo 7, MnOOH and galena particles from Herculaneum residential soils.



20µm
BEI EPA

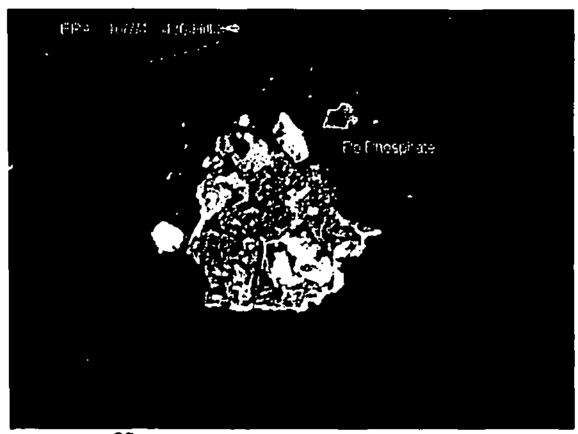
20µm
BEI EPA



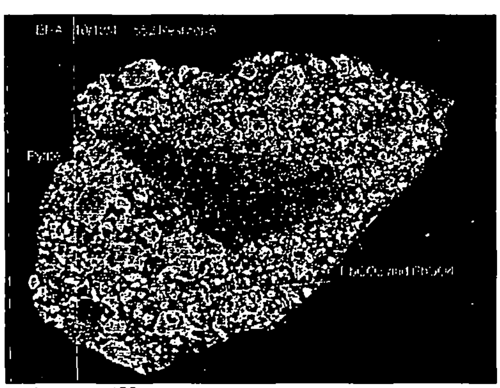
40µm
BEI EPA

Photo 8. Phosphate and other lead forms from Herculaneum residential soils.

30µm
BEI EPA



20µm
BEI EPA



400µm
BEI EPA

4.5 Atmospheric Dust

Ten atmospheric dust samples were collected by the State of Missouri, sampling stations are located on Figure 1. These samples have lead masses almost exclusively (85% of the relative lead mass) dominated by galena (PbS) and anglesite ($PbSO_4$) with minor contributions from other lead forms, Figure 4.8, Table 4.11 . The particle- size distribution for all lead species is normally distributed with a mean of approximately 4 microns, Photo 9 . The dust samples contain source-traceable lead forms providing good evidence that facility activity contributed to the elevated lead concentrations.

As with interior dust, atmospheric dust show a greater proportion of galena contributing to their lead speciation than is observed in residential soils. This may be do to the fact that post emplacement alteration/weathering is limited for both dust samples and it would also suggest that the pathway for household dust is dominated by recent, air infiltration and not by foot-traffic from residential yards.

Figure 4.8. Speciation Summary of Atmospheric Dust Samples.

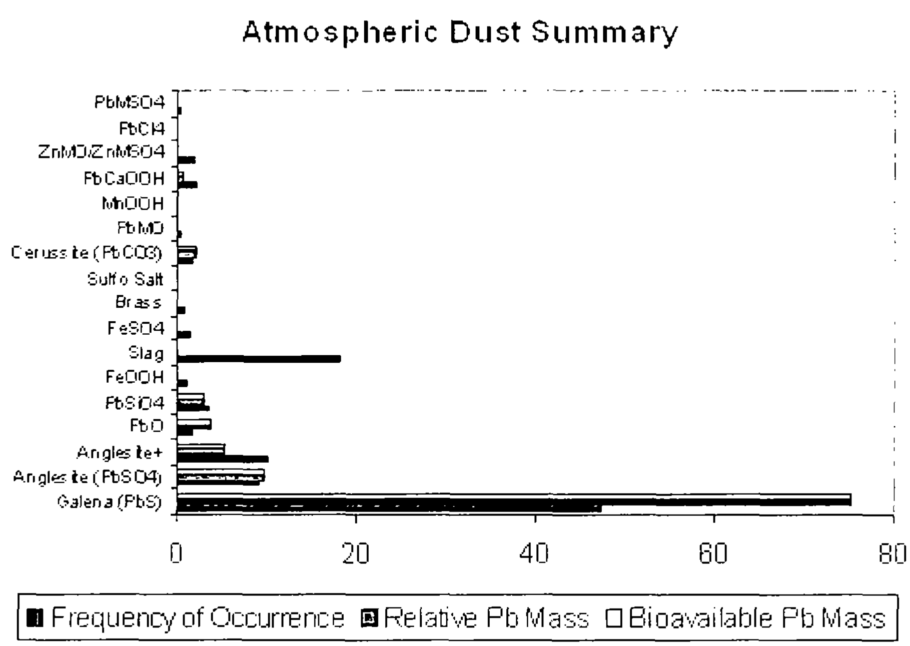
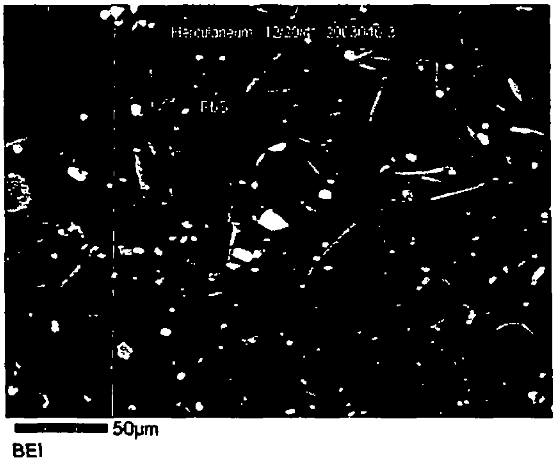
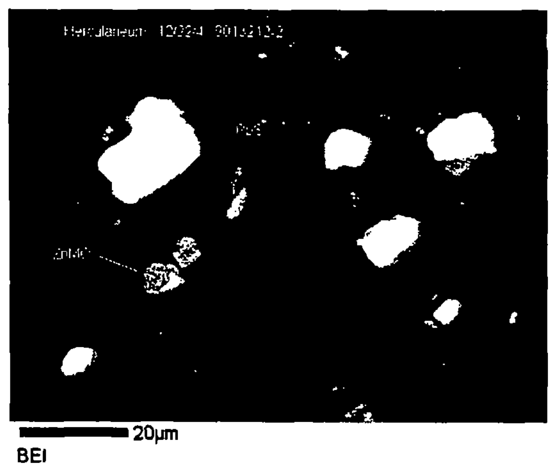


Photo 9. Galena and other lead forms from Herculaneum atmospheric dust.





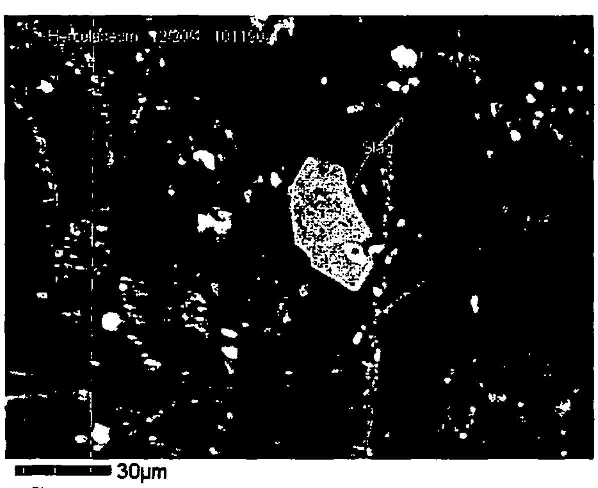


Table 4.11. Speciation of Atmospheric Dust Samples.

Sample	Form	F	F-Bio	Rm	BioRm	Error-95%	Mean Particle Size
		%	%	%	%		Microns
1011900							
	Galena	22.79	57.22	67.62	67.62	8.11	2.04
	Anglesite	3.26	12.41	9.73	9.73	5.4	3.77
	Anglesite+	4.02	4.81	1.37	1.37	3.51	6.33
	PbO	8.97	12.66	20.35	20.35	5.45	4.17
	PbSiO4	0.32	1.27	0.92	0.92	1.83	5
	FeOOH	1.32	2.03	Tr	Tr	2.31	8
	Slag	59.32	9.62	0.02	0.02	4.83	19
2003046							
	Galena	18.44	83.78	97	97	5.77	2.09
	FeSO4	0.05	0.8	0.04	0.04	1.39	3
	Anglesite+	2.29	5.05	2.05	2.05	3.43	6.33
	Anglesite	0.12	1.06	0.82	0.82	1.6	4
	Brass	79.1	9.31	0.09	0.09	4.54	35
3003047							
	Anglesite	3.31	9.74	11.79	11.92	4.04	3.2
	Galena	17.97	29.38	54.71	54.2	6.25	3.52
	Anglesite+	62.06	53.88	32.07	32.43	6.81	2.85
	PbSiO4	0.45	1.22	1.37	1.38	1.49	4
	Slag	16.02	5.18	0.06	0.06	3.02	11.33
	Sulfo Salt	0.19	0.61	Tr	Tr	1.06	4
3018793							
	Galena	2.31	30.28	80.8	80.8	7.72	3.67
	Anglesite	0.3	4.53	8.02	8.02	3.5	4.89
	Slag	96.12	53.86	1.07	1.07	8.38	20.12
	Cerussite	0.07	1.75	3.68	3.68	2.2	4.25
	PbSiO4	0.03	1.96	3.22	3.22	2.33	2.71
	FeOOH	0.26	2.06	0.06	0.06	2.39	6.67
	PbMO	Tr	0.1	0.11	0.11	0.54	1
	Anglesite+	0.84	4.63	2.8	2.8	3.53	9
	MnOOH	0.07	0.82	0.24	0.24	1.52	8
6778874							
	Galena	5.06	33.68	73.7	73.7	8.12	2.72
	PbSiO4	0.19	3.78	4.17	4.17	3.28	2
	PbO	0.48	2.58	7.67	7.67	2.72	3.75
	Anglesite+	1.08	7.73	5.94	5.94	4.59	3.75
	FeSO4	1.59	5.15	0.15	0.15	3.8	6
	Slag	90.3	40.38	0.65	0.65	8.43	13.06
	CaO	0.38	1.37	0.47	0.47	2	8
	Anglesite	0.92	4.98	7.23	7.23	3.74	4.83
	ZnMSO4	0.01	0.34	0.01	0.01	1.01	2
7061239							
	Galena	21.06	44.28	63.73	62.9	8.62	3.22
	Cerussite	1.71	4.36	4.75	4.88	3.5	3.43
	Anglesite	31.79	25.95	23.97	24.46	7.56	6.26
	ZnMSO4	1.91	1.63	0.03	0.03	2.17	9
	PbSiO4	4.52	2.18	1.85	1.91	2.5	12
	Slag	31.7	10.34	0.04	0.05	5.23	11.4
	Anglesite+	3.72	5.26	2.55	2.62	3.83	5.8

Sample	Form	F	F-Bio	Rm	BioRm	Error-95%	Mean Particle Size
		%	%	%	%		Microns
7061239 (con't)							
	PbCl4	0.07	0.54	0.5	0.52	1.26	3
	PbO	0.33	0.91	1.71	1.75	1.63	5
	ZnMSO4	0.34	1.45	0.02	0.03	2.05	4
	CaO	2.78	2.54	0.55	0.57	2.7	7
	PbMO	0.07	0.54	0.29	0.3	1.26	3
7061296							
	Galena	31.99	56.16	79.22	78.95	8.87	2.91
	PbMO	6.57	3.2	1.47	1.48	3.13	7
	Anglesite	2.2	4.11	3.78	3.83	3.54	3.6
	Slag	32.56	7.99	0.04	0.04	4.83	8.75
	Anglesite+	3.82	5.94	2.89	2.93	4.21	5.2
	PbCl4	1.3	1.6	Tr	Tr	2.23	7
	Cerussite	1.09	3.88	4.25	4.3	3.44	2.83
	CaO	0.92	2.05	0.3	0.3	2.53	4.5
	PbSiO4	17.41	11.87	8	8.1	5.76	8.67
	ZnMO	2.04	2.51	0.04	0.04	2.79	5.5
	ZnMSO4	0.1	0.68	0.01	0.01	1.47	3
7061528							
	Galena	61.66	66.39	82.25	82.25	7.34	4.19
	Anglesite	8.97	9.8	8.06	8.06	4.62	4.12
	PbSiO4	9.67	5.6	4.27	4.27	3.57	5.71
	Anglesite+	1.89	2.52	1.1	1.1	2.44	6
	Cerussite	2.44	3.92	3.83	3.83	3.02	3.5
	FeOOH	1.88	1.68	0.01	0.01	2	6
	FeSO4	1.27	1.12	0.06	0.06	1.64	8
	ZnMSO4	1.43	1.68	0.01	0.01	2	6
	Brass	2.13	2.1	0.02	0.02	2.23	7.5
	PbMSO4	5.57	2.8	0.16	0.16	2.56	10
	CaO	1.27	1.12	0.22	0.22	1.64	8
	Slag	1.81	1.26	0.01	0.01	1.73	9
9013212							
	PbO	1.05	4.96	10.17	10.22	3.46	2.62
	Cerussite	0.48	2.04	2.43	2.44	2.25	4.67
	ZnMO	0.38	3.07	0.05	0.05	2.75	3.5
	Galena	26.12	46.42	70.4	70.27	7.96	3.37
	PbSiO4	13.7	7.45	6.23	6.26	4.18	8.5
	ZnMSO4	7.35	4.09	0.06	0.06	3.15	9.33
	Anglesite	2.65	3.5	3.5	3.52	2.93	6
	Slag	22.06	4.67	0.05	0.05	3.36	16
	Anglesite+	15.16	7.15	3.78	3.8	4.11	12.25
	FeOOH	1.27	2.77	0.12	0.12	2.62	6.33
	FeSO4	0.04	0.44	0.03	0.03	1.05	3
	CaO	9.75	13.43	3.18	3.19	5.43	8.36

Sample	Form	F	F-Bio	Rm	BioRm	Error-95%	Mean Particle Size
9013631							
	Galena	17.84	50.48	80.83	80.98	8	3.35
	Anglesite	5.87	14.72	15.84	15.66	5.7	6.41
	Slag	71.03	20.5	0.16	0.16	6.45	18.63
	FeOOH	0.27	0.96	0.04	0.04	1.56	7
	Anglesite+	0.56	1.93	1.08	1.08	2.19	7
	ZnMSO4	1.39	3.16	0.03	0.03	2.79	7.67
	FeSO4	2.92	6.74	0.43	0.43	4	8.17
	PbSiO4	0.07	0.96	0.4	0.41	1.56	3.5
	PbO	0.05	0.55	1.19	1.2	1.18	4

F (Frequency of Occurrence), **F-Bio** (Bioaccessable Frequency), **Rm** (Relative Pb Mass) and **BioRm** (Bioaccessable Pb Mass) as defined in section 4.01. Error-95% is the counting error on the frequency estimate, based on Mosimann, 1965. Tr = trace value.

5.0 Quality Assurance/Quality Control

To assure quality control in both speciation and in vitro studies a series of limits and procedures are followed. These are reviewed below and any violations are noted and addressed.

5.1 In Vitro Standard Operating Procedure

The Relative Bioaccessability Leaching Procedure (RBLP) was used to evaluate sample bioaccessability for lead.

5.1.2 Background

An increasingly important property of contaminated media found at environmental sites is the bioavailabilty of individual contaminants. Bioavailability is the fraction of a contaminant that is absorbed by an organism via a specific exposure route. Many animal studies have been conducted to experimentally determine oral bioavailability of individual metals, particularly lead and arsenic. During the period 1989-97, a juvenile swine model developed by USEPA Region VIII was used to predict the relative bioaccessability of lead and arsenic in approximately 20 substrates (Weis and LaVelle 1991; Weis et al. 1994). The bioavailability determined was relative to that of a soluble salt (i.e. lead acetate trihydrate). The tested media had a wide range of mineralogy, and produced a range of lead and arsenic bioavailabilty values. In addition to the swine studies, other animal models (e.g. rats and monkeys) have been used for measuring the bioavailabilty of lead and arsenic from soils and paint.

Several researchers have developed in vitro tests to measure the fraction of a chemical solubilized from a soil sample under simulated gastrointestinal conditions. The in vitro tests consist of an aqueous fluid, into which the contaminant is introduced. The solution than solubilizes the media under simulated gastric conditions. Once this procedure is complete, the solution is analyzed for lead concentrations. The mass of the lead found in the filtered extract is compared to the mass introduced into the test. The fraction liberated into the aqueous phase is defined as the bioaccessable fraction of lead or arsenic in that media. To date, for lead-bearing materials tested in the USEPA swine studies, this in vitro assay has correlated well ($R^2 = 0.93$, $p= .0001$), with relative bioaccessability.

Further background on the development and validation of in vitro test systems for estimating lead *and arsenic bioaccessibility can be found in; Ruby et al. (1993, 1996); Medlin (1972); Medlin and Drexler, 1997; Drexler, 1998; and Drexler et al., 2004. Background information for the USEPA swine studies may be found in (Weis and LaVelle, 1991; Weis et al. 1994; and Casteel et al., 1997) and in the USEPA Region VIII Center in Denver, Colorado.*

5.1.3 Sample Preparation

All media were prepared for the in vitro assay by first drying (<40 °C) all samples and then sieving to < 250 μm. The <250 micron size fraction was used because this particle size is representative of that which adheres to children's hands. Samples were thoroughly mixed prior to use to ensure homogenization. Samples were archived after the study completion and retained for further analysis for a period of six months unless otherwise requested. Prior to obtaining a subsample for testing in this procedure, each sample was homogenized in its sample container by end-over-end mixing.

5.1.4 Apparatus and Materials

5.1.4.1 Equipment

The main piece of equipment required for this procedure is the extraction device. The device holds ten; 125 ml, wide-mouth, high-density polyethylene (HDPE) bottles. These were rotated within a Plexiglas tank by a TCLP extractor motor with a modified flywheel. The water bath must be filled such that the extraction bottles remained immersed. Temperature in the water bath was maintained at 37 +/- 2 °C using an immersion circulator heater (Fisher Scientific Model 730). The 125-ml HDPE bottles had an airtight screw-cap seal (Fisher Scientific #02-893-5C), and care was taken to ensure that the bottles did not leak during the extraction procedure.

5.1.4.2 Standards and Reagents

The leaching procedure for this method used an aqueous extraction fluid at a pH value of 1.5. The pH 1.5 fluid was prepared as follows:

Two liters of aqueous extraction fluid were prepared using ASTM Type II deionized (DI) water. The buffer was made up in the following manner. To 1.9 L of DI water, 60.06 g glycine (free base, reagent grade), were added bringing the solution volume to 2 L (0.4M glycine). The mixture was placed in the water bath at 37 °C until the extraction fluid reached 37 °C. The pH meter (using both a 2.0 and a 4.0 pH buffer for standardization) was standardized using temperature compensation at 37 °C or buffers maintained at 37 °C in the water bath. Trace metal grade, concentrated hydrochloric acid (12.1N) was added until the solution pH reached a value of 1.50 +/_ 0.05 (approximately 60 mL).

All reagents were free of lead and arseic, and the final fluid was tested to confirm that lead and arsenic concentrations were less than one-fourth the project required detection limit (PRDL) of 100 (less than 25 μg/L lead 5μg/L arsenic) in the final fluid.

Cleanliness of all materials used to prepare and/or store the extraction fluid and buffer is essential. All glassware and equipment used to prepare standards and reagents were properly cleaned, acid washed, and finally, triple-rinsed with deionized water prior to use. When possible, disposable "poly" tubes were used.

5.1.5 Leaching Procedure

100 +/- 0.5 mL of the extraction fluid was measured, using a graduated cylinder, and transfered to a 125 mL wide-mouth HPDE bottle. 1.00 +/- 0.5 g of test substrate (<250 m) was added to the bottle, ensuring that static electricity did not cause soil particles to adhere to the lip or outside

threads of the bottle. If necessary, an antistatic brush was used to eliminate static electricity prior to adding the media. The mass of substrate added to the bottle was recorded. Each bottle top was hand tightened and shaken/inverted to ensure that no leakage occurred, and that no media was caked on the bottom of the bottle.

The bottle was placed into the modified TCLP extractor, making sure each bottle was secure and the lid(s) were tightly fastened. The extractor was filled with 125 mL bottles containing test material or QA samples.

The temperature of the water bath was 37 +/- 2 °C.

The extractor was turned on and rotated end-over-end at 30 +/- 2 rpm for 1 hour. The start time of rotation was recorded.

When extraction (rotation) was complete, the extractor rotation was immediately stopped and the bottles were removed. They were then wiped dry and placed upright on the bench top.

Extract was removed directly from the reaction vessel into a disposable 20 cc syringe with a Luer-Lok attachment. A 0.45 μm cellulose acetate disk filter (25 mm diameter) was attached to the syringe, and the extract was filtered into a clean 15 mL polypropylene centrifuge tube (labeled with sample ID) or other appropriate sample vial for analysis.

The time that the extract was filtered was recorded (i.e. extraction was stopped). If the total time elapsed was greater than 1 hour 30 minutes, the test was repeated.

The pH of the remaining fluid was measured in the extraction bottle. If the fluid pH was not within +/- 0.5 pH units of the starting pH, the test was discarded and the sample reanalyzed as follows:

If the pH had changed more than 0.5 units, the test was re-run in an identical fashion. If the second test also resulted in a decrease in pH of greater than 0.5 s.u. this was recorded, and the extract filtered for analysis. If the pH had increased by 0.5 s.u. or more, the test was repeated, but the extractor stopped at specific intervals and the pH manually adjusted down to pH of 1.5 with dropwise addition of HCl (adjustments at 5, 10, 15, and 30 minutes into the extraction, and upon final removal from the water bath { 60 min}). Samples with rising pH values might better be run following the method of Medlin, 1997.

Filtered samples were stored in a refrigerator at 4 °C until analyzed. Analysis for lead and arsenic concentrations occurred within 1 week of extraction for each sample.

In general, extracts were analyzed for lead and arsenic, following EPA methods 6010B, 6020, or 7061A.

5.1.6 Quality Control/Quality Assurance

Quality Assurance for the extraction procedure consisted of a series of quality control samples.

Controls, control limits and corrective actions are listed in Table 5.1.6.1 .

Table 5.1.6.1.

	Analysis Frequency	*Control Limits*	*Corrective Actions*
Reagent Blank	*once per batch*	*< 25 µg/L lead*	*Make new fluid and re-run all analyses.*
Bottle blank	*1 in 10*	*<50 µg/L lead*	*Check calibration and re-analyze as necessary.*
Blank spike*	*1 in 10*	*85-115% recovery*	*Check calibration and/or source of contamination and re-analyze.*
Matrix spike*	*1 in 20*	*75-125% recovery*	*Flag*
Duplicate sample	*1 in 20*	*+/- 20% RPD***	*Flag*
Control soil***	*1 in 25*	*+/- 10% RPD*	*Flag*

- *Spikes contained 10 mg/L lead . ** RPD= relative percent difference.*
- **** The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) RPD is based upon mean RBA-lead values of 84% and 75% for MS2711 and MS2710, respectively.*

5.1.7 Bulk Soil Analyses

Analysis of the <250 µ soil sample was carried out using Good Laboratory Practice (GLP) protocols. Samples were digested following EPA Method 3050B. Analysis of the digest was similar to EPA Methods 6020 A or B, but with somewhat reduced QA/QC. Controls, control limits and corrective actions are listed in Table 5.1.7.1. Initial calibration was based on a 4- point calibration curve with a minimum 0.999 R^2 value.

Table 5.1.7.1.

	Analysis Frequency	*Control Limits*	*Corrective Actions*
Method Blank	*once per run*	*25 µg/L lead*	*Check calibration and/or source of contamination and re-analyze all samples.*
IVC Initial Calibration Verification	*once per run*	*90-110% recovery*	*Check calibration and start run over.*
Interference Check	*once per run*	*90-110% recovery*	*Flag*
Matrix spike*	*1 in 20*	*75-125% recovery*	*Flag*
CCV Continuing Calibration Verification	*1 in 10*	*90-110% recovery*	*Check calibration and re-analyze preceding samples.*
Duplicate sample	*1 in 20*	*+/- 20% RPD*	*Flag*

* *Spikes contained 1000 mg/L lead*

5.1.8 QA/QC Data Evaluation

Data evaluation is based on in vitro analyses from the current set of samples, not historical samples that have been added to this report for comprehensiveness. Bulk soil analyses met or exceeded most required QA/QC. Observed elevation in method some method blanks exceeded limits, but were determined acceptable and therefore no corrective action was necessary. Results are summarized below.

3050B	***Analysis Frequency***	***Control Limits***	***Corrective Actions***
Method Blank	*3 Method blank run*	*two values above limit.*	*Control limits set for ICP/MS-samples run by ICP/AES. All other procedural blanks low. No Action taken*
IVC Initial Calibration Verification	*once per run*	*99% recovery*	*None*
Interference Check	*once per run*	*99% recovery*	*None*
CCV Continuing Calibration Verification	*3 CCV run*	*95-98% recovery*	*None*
Matrix spike	*2 matrix spike run*	*87-95% recovery-Pb*	*None*
Duplicate sample	*3 duplicates run*	*1-3% RPD-Pb*	*None*

RBLP analyses did not meet all QA/QC, however, the observed violation would not effect the data quality and no corrective action is suggested.

RBLP	***Analysis Frequency***	***Control Limits***	***Corrective Actions***
Reagent Blank	*One Reagent Blank*	*<1 µg/L lead*	*None*
Bottle blank	*3 blank run*	*<20 µg/L lead*	*None*
Blank spike	*3 blank spikes run*	*99% recovery*	*None*
Matrix spike	*3 matrix spikes run*	*35,95, 200 (77)% recovery*	*Two spike recoveries outside control limits for lead only. One of the two would have fallen into limits if procedure duplicate concentration used to calculate % recovery. Both failed samples are very high in Pb thus higher RPD anticipated. Other metals showed good recovery. Other QA very good so No action taken.*
Duplicate sample	*3 duplicates run*	*1,2, 10% RPD*	*None*
Control soil	*1 control run*	*2% RPD*	*None*

Table 5.12

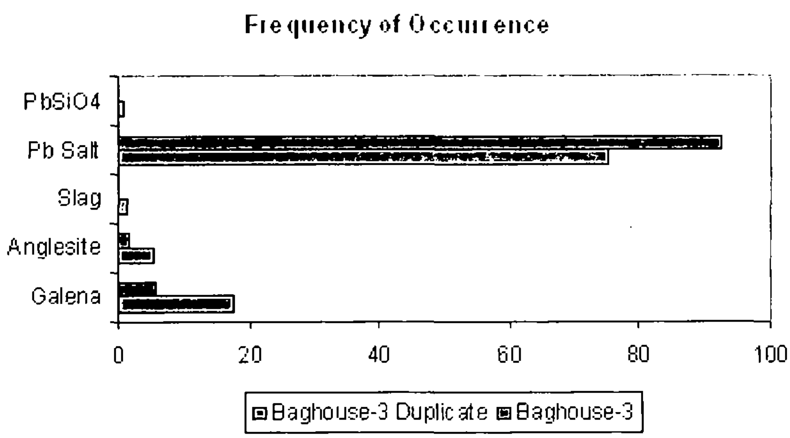
QA Summary Of In Vitro Bioassay Results for Lead

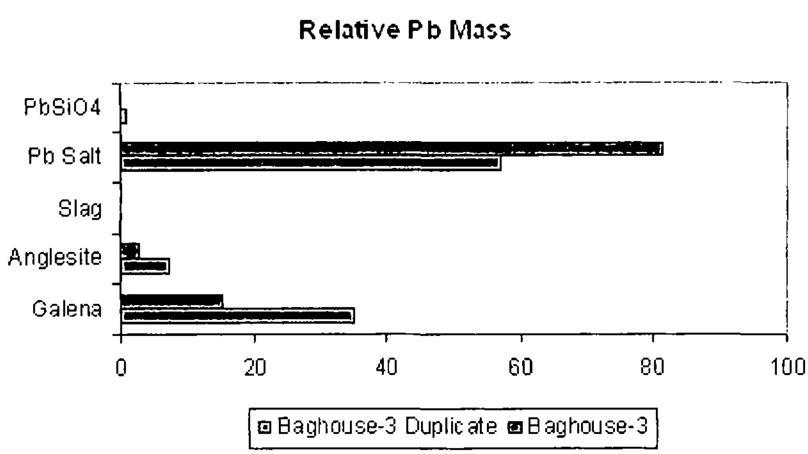
Sample		mass soil (g)	ICP Pb (mg/l)	Pb in bulk soil mg/kg	% Relative Pb Bioavailability
425-HILL-PROC-DUP		2093.93	1.00732	17.54	83
HLS-RD-4-AD		14783.02	0.99948	58.98	40
HLS-RD-1-DUP		132318.33	0.55961	200.04	27
BHG-6-PROC-DUP		444480.38	0.54802	1106.660	45
NIST-2711		1162.00	1.01927	10.18	86
BLANK-1				0.38	
BLANK-1				-0.24	
BLANK-2				-0.04	
BLANK-3				0.16	
BLANK-1-SPK	(10 ppm)			10.04	
BLANK-1-SPK	(10 ppm)			10.52	
BLANK-2-SPK	(10 ppm)			10.02	
BLANK-3-SPK	(10 ppm)			10.22	
BHG-6-SPK	(10 ppm)	444480.38	0.48719	1098.96	
HLS-RD-1-SPK	(10 ppm)	132318.33	0.50105	185.34	
425-HILL-SPK	(10 ppm)	2093.93	1.00554	26.9	

5.2 QA/QC of Speciation Analysis.

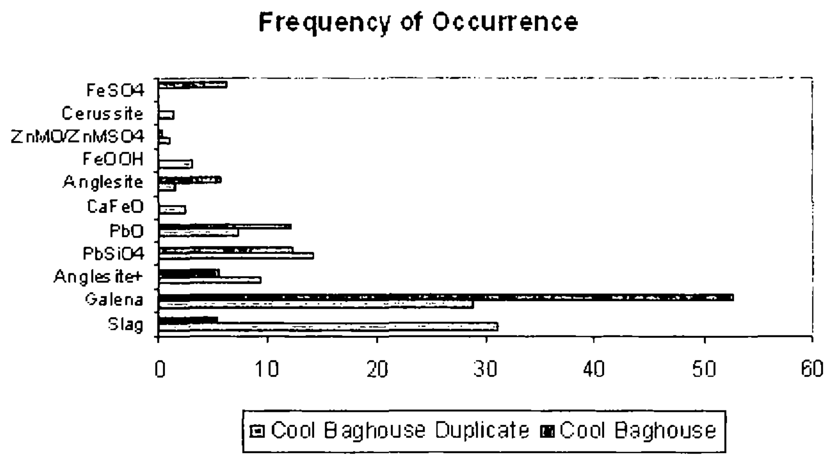
The primary quality control procedure for the speciation analysis is the analysis of duplicate samples at a 10% frequency. A representative sample split from a single sample is taken, prepared and analyzed following the speciation SOP to produce the duplicate results. Although variations in sample duplicates are observed, in all cases the major (both in frequency of occurrence and relative lead mass) forms of lead are similar. The dominant relative lead mass phase is always (100%) identified as the same phase, while the dominant order to frequency of occurrences varies about 50% of the time. A comparison of duplicate analyses is provided in Figure 5.2.1. The frequency of occurrence for the dominant lead forms average 30% RPD (ranging from 4-58%), while the relative lead mass estimates average 19% RPD (ranging from 2-31%), All observed variations are considered acceptable, thus no corrective action is required.

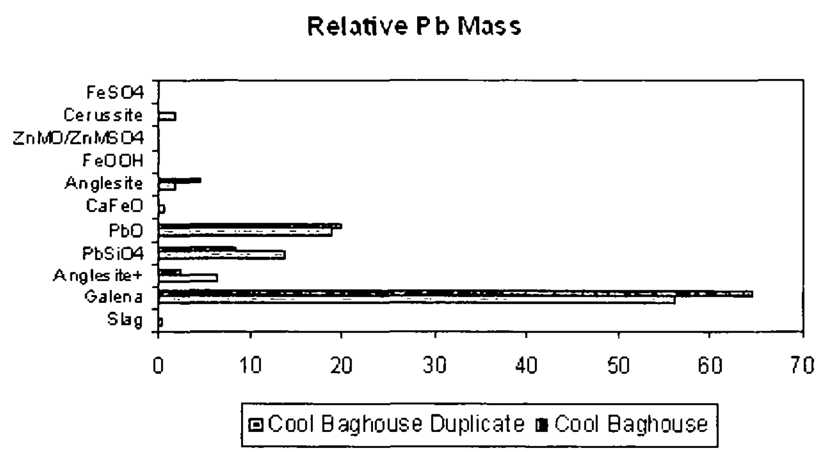
Baghouse-3


Frequency of Occurrence
PbSiO4
Pb Salt
Slag
Anglesite
Galena
0
20
40
60
80
100
Baghouse-3 Duplicate
Baghouse-3

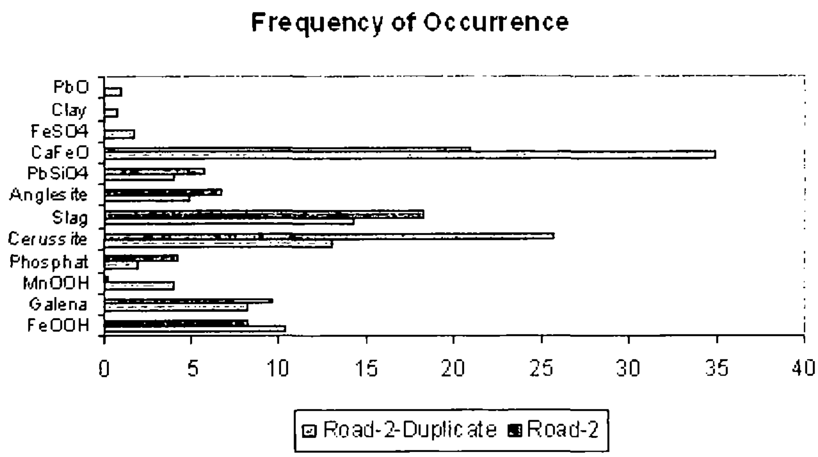

Relative Pb Mass
PbSiO4
Pb Salt
Slag
Anglesite
Galena
0
20
40
60
80
100
Baghouse-3 Duplicate
Baghouse-3

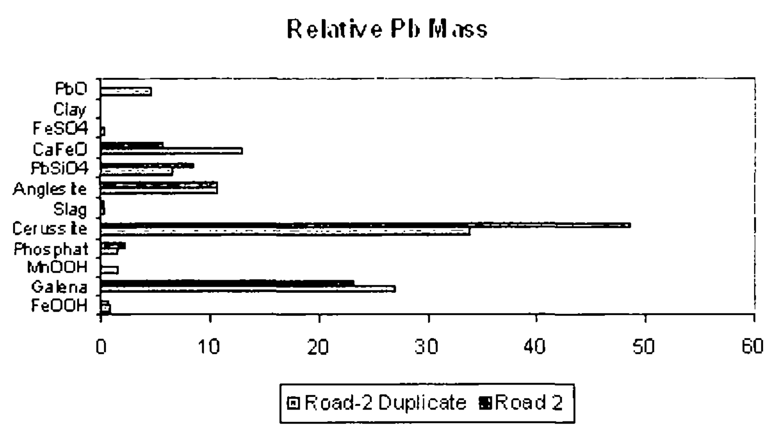
Cooler Baghouse



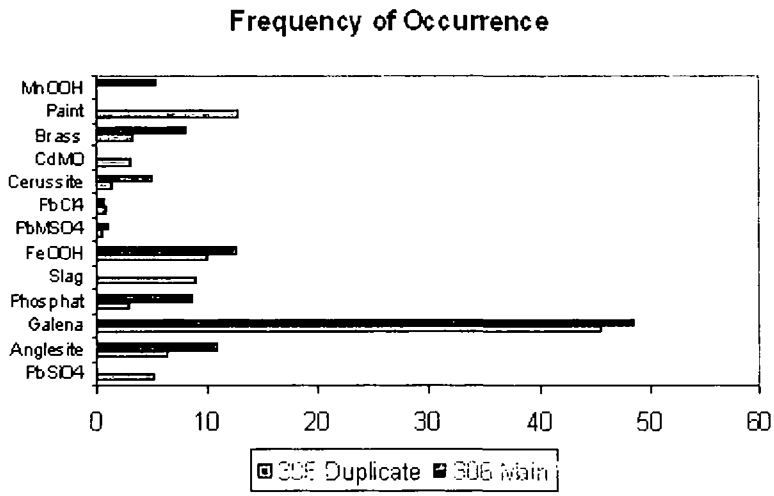


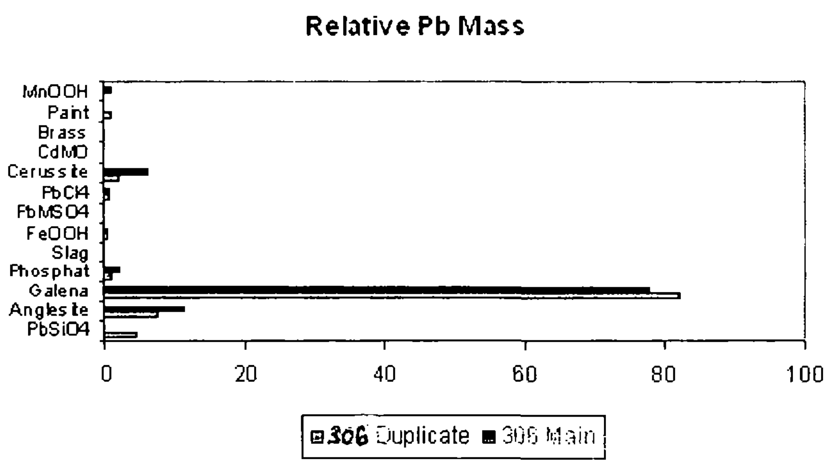
Roadside -2


Frequency of Occurrence
PbO
Clay
FeSO4
CaFeO
PbSiO4
Anglesite
Slag
Cerussite
Phosphat
MnOOH
Galena
FeOOH
0
5
10
15
20
25
30
35
40
Road-2-Duplicate
Road-2


Relative Pb Mass
PbO
Clay
FeSO4
CaFeO
PbSiO4
Anglesite
Slag
Cerussite
Phosphat
MnOOH
Galena
FeOOH
0
10
20
30
40
50
60
Road-2 Duplicate
Road 2

306 Main Dust





6.0 BIOACESSABILITY

The relative bioacessability for both facilities, roadside, dust and residential samples was determined using the Relative Bioacessability Leaching Procedure (RBLP) developed at the University of Colorado, Drexler et. al., 2005, USEPA, 2004. The procedure predicts gastrointestinal bioavailabity of lead. It has been calibrated to the USEPA Region VIII swine model and has been independently validated. Results of the test are provided in Table 6.13 and graphically presented in Figure 6.9. Data are generally consistent with the speciation results presented in this report averaging 36% in vitro relative bioacessability (IVRBA) for facility media, 57% IVRBA for dusts, 45% IVRBA for roadside soils, and 81% IVRBA for residential soils. This increase in residential IVRBA is consistent with the oxidation of facilities sulfide (generally low IVRBA).

Figure 6.9. Herculaneum RBA vs Lead Concentration.

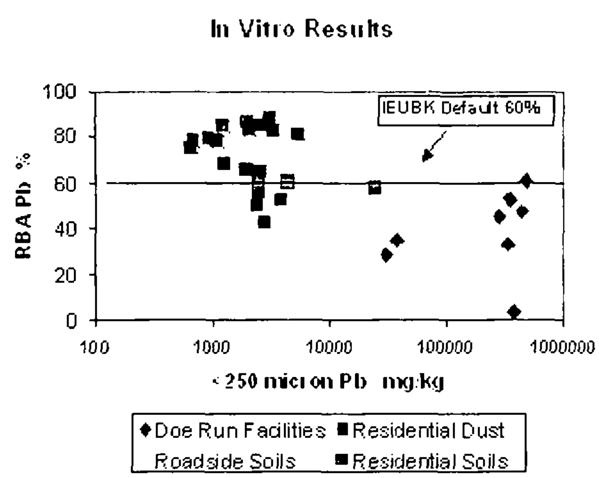


Table 6.13. Herculaneum In Vitro Bioassay Results.

Sample	Pb in bulk soil mg/kg	mass soil (g)	calc Pb #1	ICP Pb (mg/l)	solution amt (l)	% Relative Pb Bioavailability
Facilities Samples						
HLS-SLAG-1	30488.25	1.00552	30.65654	88.54	0.1	28
HLS-SLAG-2	37906.48	1.00358	38.04141	131.320	0.1	35
TC-1	374192.43	1.00585	376.30681	128.54	0.1	3
TC-2	379797.07	1.01395	385.09524	116.94	0.1	3
CBH-1	343470.08	0.58806	201.98101	1068.980	0.1	53
ESP-1	281830.77	0.50036	141.01684	635.300	0.1	46
BHG-3	335157.78	0.57907	194.07981	638.32	0.1	33
BHG-5	483094.61	0.53558	258.72615	1568.800	0.1	61
BHG-6	444480.38	0.51361	228.28957	1078.38	0.1	47
BHG-7	352684.16	0.54019	190.51648	1000.26	0.1	53
Dusts						
430-D-HILL	1940.11	1.00784	1.95532	12.78	0.1	65
320-D-CURVED	2541.91	1.00347	2.55073	16.38	0.1	64
515-D-THURWELL	1271.76	1.0159	1.29199	8.78	0.1	68
835-D-CROSS	24650.99	1.00598	24.79840	142.32	0.1	57
552-D-RESERVIOR	2477.56	1.00832	2.49817	13.86	0.1	55
906-D-CHURCH	3851.86	1.01042	3.89200	20.28	0.1	52
306-D-MAIN	2786.81	1.0066	2.80520	11.86	0.1	42
511-D-LONG	2393.83	1.00773	2.41234	11.94	0.1	49
785-D-CIRCLE	4395.01	0.99311	4.36473	26.22	0.1	60
774-D-CIRCLE	2468.49	1.01166	2.49782	14.6	0.1	58
Roadways						
HLS-RD-1	132318.33	0.50947	67.41222	181.78	0.1	27
HLS-RD-2	16085.96	1.0107	16.25808	124.86	0.1	77
HLS-RD-3	28472.12	1.01105	28.78674	102.9	0.1	36
HLS-RD-4	14783.02	0.99948	14.77533	58.96	0.1	40
Soils						
836-CROSS	2838.61	1.01314	2.87329	22.52	0.1	84
517 LONG	3088.58	1.00976	3.11870	27.16	0.1	87
515 THURWELL	1240.13	1.0033	1.24422	10.44	0.1	84
928-CHURCH	865.26	1.00113	0.86602	4.94	0.1	74
306-MAIN	3332.34	1.0034	3.34367	27.38	0.1	82
522-RESERVIOR	5483.59	1.00543	5.51337	44.2	0.1	80
624-BROWN	1111.76	1.00891	1.12168	8.68	0.1	77
430-HILL	2456.60	1.01182	2.48564	20.98	0.1	84
425-HILL	2093.93	1.00416	2.10264	17.32	0.1	82
511-LONG	1992.15	1.01036	2.01277	17.3	0.1	86
300-ST-LOUIS	697.90	1.00491	0.70133	5.42	0.1	77
351-SHORT	939.92	1.01048	0.94977	7.46	0.1	79

7.0 CONCLUSIONS

Based on the data presented in this summary the following conclusions can be reached with respect to the occurrences of lead found in residential soils and dusts from the Herculaneum area.

- *Soils have elevated RBA values with respect to the IEUBK default values and are consistent with the elevated blood leads observed at the site.*

- *Yards and house dust have "fingerprinting" forms, many of these are common to the Doe Run facility.*

- *Neither paint nor gasoline are significant lead contributors to the site.*

Based on the data reviewed in this summary it is my opinion that the lead in residential soils and house dust from the Herculaneum area are the result of activities associated with the Doe Run operation and include; smelter-stack emissions, fugitive emissions from hauling and storage as well as waste and concentrate spillages.

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APPENDIX 1

Chain-of-Custody Forms

Table 1.0A

8.24.05

BLACK & VEATCH
SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.: 46918

PROJECT NAME: Herculaneum Lead Smelter

SAMPLERS: (Signature) Sarah Howard   Bridget K. Bolin

STA. NO.	DATE	TIME	COMP.	GRAB	SAMPLE ID ~~STATION LOCATION~~	NO. OF CON-TAINERS	SOIL SAMPLE	Speciation-Pb	In-vitro analysis	Total Pb			REMARKS
N/A	8.25.04	0952	X		HLS-SS-515 Thurwell-CU	1	X	X	X	X			
	8.24.04	0926	X		HLS-SS-430 Hill-CU	1	X						
	8.30.04	0932	X		HLS-SS-824 Brown-CU	1	X						
	8.25.04	1040	X		HLS-SS-351 Short-CU	1	X						
	8.26.04	1028	X		HLS-SS-306 Main-CU	1	X						
	8.25.04	1051	X		HLS-SS-835 Cross-CU	1	X						
	8.24.04	0930	X		HLS-SS-425 Hill-CU	1	X						
	8.26.04	1204	X		HLS-SS-300 St. Louis-CU	1	X						
	8.24.04	1245	X		HLS-SS-517 Long-CU	1	X						
	8.30.04	1000	X		HLS-SS-928 Church-CU	1	X						
	8.24.04	1245	X		HLS-SS-511 Long-CU	1	X						
	8.24.04	10:35	X		HLS-SS-552 Reservoir-CU	1	X						

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Sarah Howard	9/2/04 1400				

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)

Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks

Distribution: White and Yellow Accompanies Shipment; Pink copy to Field Files

8

BLACK & VEATCH
SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.: 46918

PROJECT NAME: Herculaneum Lead Smelter

SAMPLERS: (Signature) Sarah Howard Bridget K. Belin

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	Pb Speciation	In-vitro Analysis	Total Pb				REMARKS
N/A	8/23/04	1525		X	HLS-VB-430 Hi... -EPA	1	X	X	X				Vacumn Bag Dust Samples
	8/24/04	1640			HLS-VBD-515 Thurnell-EPA	1							
	8/24/04	1038			HLS-VBD-552 Reservoir-EPA	1							
	8/24/04	1233			HLS-VBD-511 Long-EPA	1							
	8/25/04	1051			HLS-VBD-835 Cross-EPA	1							
	8/24/04	1014			HLS-VBD-306 Main-EPA	1							
	8/31/04	1324			HLS-VBD-905 Church-EPA	1							
	8/31/04	1344			HLS-VBD-785 Circle-EPA	1							
	8/31/04	1349			HLS-VBD-774 Circle-EPA	1							
	9/1/04	0930			HLS-VBD-320 Curved-EPA	1							

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Sarah Howard	9/2/04 1400				

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)

Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks

Distribution: White and Yellow Accompanies Shipment; Pink copy to Field Files

8145

BLACK & VEATCH
SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
46918	Herculaneum Lead Smelter

SAMPLERS: (Signature) Sarah Howard   Bridget K. Bolin

STA. NO.	DATE	TIME	COMP.	GRAB	SAMPLE ID ~~STATION LOCATION~~	NO. OF CON-TAINERS	Pb Speciation	In-vitro analysis	Total Pb			REMARKS
N/A	8/24/04	0655		X	HLS-RD-1-CU	1	X	X	X			Road dust: btwn concentrate dump area and deco
	8/30/04	0835		X	HLS-RD-2-CU	1						Station St. Composite
		0848		X	HLS-RD-3-CU	1						Main St. Composite
		0815		X	HLS-RD-4-CU	1						Joachim St. Composite
	8/24/04	0640		X	HLS-TC-1-CU	1						Truck Lead concentrate
	"	0650		X	HLS-TC-2-CU	1						" " "
	8/23/04	0953		X	HLS-SLAG-1	1						Slag Pile
		1005		X	HLS-SLAG-2	1						"
		1118		X	HLS-CBH-1	1						Cooler Bag House
		1143		X	HLS-BH5-1	1						Bag House 5
		1105		X	HLS-BH3-1	1						Bag House 3
		1216		X	HLS-BH7-1	1						Bag House 7
		1155		X	HLS-ESP-1	1						Electro Static Precipitator
		1210		X	HLS-BH6-1	1						Bag House 6

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Bridget K. Bolin	9/2/04 1400				

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)

Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks

Distribution: White and Yellow Accompanies Shipment; Pink copy to Field Files

Table 1.0A
Specific Gravity and Concentration Factors for Lead Phases

	Specific Gravity	Pb ppm
Clay	3.1	20,000
BiMO	9	50,000
Brass	5.5	10,000
CrMO	4.5	26,000
CuMSO4	4	128,000
FeOOH	4	45,000
MnOOH	5	142,000
NbTiPb	6	385,000
Organic	1.3	57,000
Paint	6	45,000
PbAsO	7.1	500,000
PbCaO	6	170,000
PbCl4	5.85	740,000
PbCrO4	6.4	450,000
PbMO	6.5	385,000
Phosphate	5	298,000
Slag	3.65	13,700
Sulfo-Salt	5	250,000
FeSO4	3.7	15,000
ZnMO/SO4	4	20,000
PbSnSO4	6	128,000
PbMSO4	6	200,000
PbSnCl	6	265,000
PbSolder	6.3	73,000
PbVO	6.4	320,000
PbSiO4	6.5	500,000
Pb-Salt	6	410,000
PbSiO4	6.5	500,000
Anglesite+	6	380,000
CaPbSO4	3.5	80,000
CaFeO	3.5	210,000
Cerussite	6.6	776,000
Galena	7.5	866,000
Anglesite	6.3	684,000
PbO	9.5	930,000

Data is either site-specific, based on average EMPA quantitative analyses or Dana's Mineralogy and/or Handbook of Chemistry.

METAL SPECIATION SOP

1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to specify the proper methodologies and protocols to be used during metal speciation of various solid samples including; tailings, slags, sediments, dross, bag house dusts, wipes, paint, soils, and dusts for metals. The metal speciation data generated from this SOP may be used to assess the solid samples as each phase relates to risk. Parameters to be characterized during the speciation analyses include particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. This electron microprobe (EMP) technique, instrument operation protocols and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

2.0 BACKGROUND

To date, numerous metal-bearing forms have been identified from various environments within western mining districts (Emmons et al., 1927; Drexler, 1991 per. comm.; Drexler, 1992; Davis et al., 1993; Ruby et al., 1994; CDM, 1994; WESTON, 1995), and industrial or agricultural (Drexler , 1999 per. comm.) settings, Table 2-1. This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms are minerals with varying metal concentrations (e.g., lead phosphate, iron-lead oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (e.g., lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It may be important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 microns (μm) are most available for human ingestion and/or inhalation (Bornschein, et al., 1987). For this study, the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined, it has been shown (CDM, 1994) that data collected on particle area produces similar results. These measurements add a considerable amount of time to the procedure, introduce new sources of potential error and limit the total number of particles or samples that can be observed in a study.

- **free or liberated**
- **inclusions within a second phase**
- **cementing**
- **alteration rims**

3.0 SAMPLE SELECTION

Samples should be selected and handled according to the procedure described in the Project Plan.

4.0 SCHEDULE

A schedule for completion of projects performed under this Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

5.0 INSTRUMENTATION

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder or other comparable facilities. Primary equipment used for this work will include:

Electron Microprobe (JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and Geller Microanalytical data processing system. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses are essential.

6.0 PRECISION AND ACCURACY

The precision of the EMP speciation and polarized light microscopy (PLM) will be evaluated based on sample duplicates analyzed at a frequency of 10%. The precision of the data generated by the manual PLM particle count and by the "EMP point count" will be evaluated by preparing a graph that compares the original result with the duplicate result. The accuracy of the analyses will be estimated based on a number of methods, depending on the source of the data. Data generated by the "EMP point count" or will be evaluated statistically based on the methods of Mosimann (1965) at the 95% confidence level on the frequency data following Equation 1.

$$E_{0.95} = 2P(100\text{-}P)/N \qquad \text{(Eq. 1)}$$

Where: $E_{0.95}$ = Probable error at the 95% confidence level

P = Percentage of N of an individual metal-bearing phase based on percent length frequency

N = Total number of metal-bearing grains counted

In general, site-specific concentrations for these variable, metal-bearing forms will be determined by performing "peak counts" on the appropriate wavelength spectrometer. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced databases or estimated based on similar compounds.

7.0 PERSONNEL RESPONSIBILITY

The analysts will carefully read this SOP prior to any sample examination.

It is the responsibility of the laboratory supervisor and designates to ensure that these procedures are followed, to examine quality assurance (QA) samples and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the contractor.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses sheets (DAS), will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the contractor representative of any problems encountered in the sample analysis process.

8.0 SAMPLE PREPARATION

Grain mounts (1.5 inches in diameter) of each sample will be prepared using air-cured epoxy. This grain mounting technique is appropriate for most speciation projects, however polished thin-sections, paint chips, dust wipes, or filters may be prepared in a similar manner. The grain mounting is performed as follows:

1) Log the samples for which polished mounts will be prepared.

2) Inspect all disposable plastic cups, making sure each is clean and dry.

3) Label each "mold" with its corresponding sample number.

4) All samples will be split to produce a homogeneous 1-4 gram sample.

5) Mix epoxy resin and hardener according to manufacturer's directions.

6) Pour 1 gram of sample into mold. Double check to make sure sample numbers on mold and the original sample container match. Pour epoxy into mold to just cover sample grains.

7) Use a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.

8) Set molds to cure at ROOM TEMPERATURE in a clean restricted area. Add labels with sample numbers and cover with more epoxy resin. Leave to cure completely at room temperature.

9) One at a time remove each sample from its mold and grind flat the back side of the mount.

10) Use 600 grit wet abrasive paper stretched across a grinding wheel to remove the bottom layer and expose as many mineral grains as possible. Follow with 1000 grit paper.

11) Polish with 15 um oil-based diamond paste on a polishing paper fixed to a lap. Use of paper instead of cloth minimizes relief.

12) Next use 6um diamond polish on a similar lap.

13) Finally polish the sample with 1um oil-based diamond paste on polishing paper, followed by 0.05 um alumina in water suspension. The quality should be checked after each step. Typical polishing times are 30 minutes for 15 um, 20 minutes for 6 um, 15 minutes for 1 um, and 10 minutes for 0.05 um.

NOTE: use low speed on the polishing laps to avoid "plucking" of sample grains.

14. Samples should be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and fingerprints.

15. To ensure that no particles of any metal are being cross-contaminated during sample preparation procedures, a blank (epoxy only) mold will be made every 25th sample following all of the above procedures. This mold will then be speciated along with the other samples.

Each sample must be carbon coated. Once coated, the samples should be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

9.0 Concentration Pre-screening

All samples will be initially examined using the electron microprobe to determine if the number of particles are too great to obtain a representative count. The particle counting will be considered representative if the entire sample (puck) has been traversed about the same time in which the counting criteria are achieved.

If this examination reveals that one metal is abundant (> 1% of total metals concentration), clean quartz sand (SiO_2) will be mixed with the sample material. The sand should be certified to be free of target analytes. The quartz sand should be added to an aliquot of the investigative sample, then mixed by turning the sample for a minimum of one hour, or until the sample is fully homogenized. The initial mass of the investigative sample aliquot, and the mass of the quartz addition must be recorded on the Data Analysis Sheet (DAS).

10.0 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours will be spent on each analysis.

10.1 Data Reduction

Analysts will record data as they are acquired from each sample using the LEGS software, (Figure 10-1) which places all data in a spreadsheet file format. Columns have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, C= cementing, R = rimming, I = included). The analyst may also summarize his/her observations in the formatted data summary files.

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency bar-graph. The particle size distribution of metal-bearing forms will be depicted in a histogram. Size-histograms of each metal-bearing form can be constructed from data in the file.
Data from EMP will be summarized using two methods. The first method is the determination of FREQUENCY OF OCCURRENCE. This is calculated by summing the longest dimension of all the metal-bearing phases observed and then dividing each phase by the total.
Equation 2 will serve as an example of the calculation.

$$F_M \text{ in phase-1} = \frac{\Sigma(\text{PLD})_{\text{phase 1}}}{\Sigma(\text{PLD})_{\text{phase-1}} + \Sigma(\text{PLD})_{\text{phase-2}} + \Sigma(\text{PLD})_{\text{phase-n}}} \qquad \text{(Eq. 2)}$$

Where:
F_M = Frequency of occurrence of metal in a single phase.
PLD = An individual particle's longest dimension
$\%F_M$ in phase-1 = F_M in phase-1 * 100

These data thus illustrate which metal-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report is the determination of RELATIVE METAL MASS. These data are calculated by substituting the PLD term in the equation above with the value of M_M. This term is calculated as defined below.

$$M_M = FM * SG * ppm_M \qquad \text{(Eq. 3)}$$

Where:
M_M = Mass of metal in a phase
SG = Specific Gravity of a phase

ppm_M = Concentration in ppm of metal in a phase

The advantage in reviewing the RELATIVE METAL MASS determination is that it gives one information as to which metal-bearing phase(s) in a sample are likely to control the total bulk concentration for a metal of interest. For example, PHASE-1 may comprise 98% relative volume of the sample; however, it has a low specific gravity and contains only 1,000 parts per million (ppm) arsenic. PHASE-2 comprised 2% of the sample, has a high specific gravity, and contains 850,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

Finally, a concentration for each phase is calculated. This quantifies the concentration of each metal-bearing phase. This term is calculated as defined below (Eq. 4).

$$ppm_M = M_M * \text{Bulk metal concentration in ppm} \qquad \text{(Eq. 4)}$$

10.2 Analytical Procedure

A brief visual examination of each sample will be made, prior to EMP examination. This examination may help the operator by noting the occurrence of slag and/or organic matter. Standard operating conditions for quantitative and qualitative analyses of most metal-bearing forms are given in Table 8-1. However, it is the responsibility of the operator to select the appropriate analytical line (crystal/KeV range) to eliminate peak overlaps and ensure proper identification/quantification of each analyte. Quality control will be maintained by analyzing duplicates at regular intervals (Section 8.5).

The backscattered electron threshold will be adjusted so that all particles in a sample are seen. This procedure will minimize the possibility that low metal-bearing minerals may be overlooked during the scanning of the polished grain mount. The scanning will be done manually. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2 um) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on an EMP, with spectrometers typically peaked at sulfur, oxygen, carbon and the metal(s) of concern (M). The size of each metal-bearing phase will be determined by measuring in microns the longest dimension.

10.3 Compound Identification

As outlined in the EMPA SOP, an electron microprobe with combined EDS (energy dispersive spectrometer) and multiple WDS (wavelength dispersive spectrometers) are used to identify all metal-bearing phases of interest. A 1-2 gram split of dryed sample is placed in a 2.5 cm plastic mold and impregnated with epoxy. Once the sample is hardened it is polished and carbon coated for EMPA. The EMPA is operated at 15 kV accelerating voltage, with a 20 NanoAmp current and a 1 micron focused beam. Elements of interest are standardized using certified mineral or pure metal standards and counting times are chosen to provide 3-sigma detection limits of between 100-200 ppm. Elemental concentrations are corrected using ZAF factors and concentration errors are generally less than 5% relative. For a more detail explanation of the EMPA method of analyses see Birks, 1971, or Heinrich, 1981.

Although the electron microprobe is capable of determining stoichiometries of virtually any compound composed of elements Be thru U, such a task requires a great deal of standardization and analytical time to complete. It has been determined that for the purposes these data are utilized in either risk assessments or site characterizations the term "speciation" would have a more general definition. The primary justification for this factor is that it has been shown the time required for more precise phase identification greatly impacted on the total identified-particle population. The significance to the data interpretation is highly dependent on the total number of metal-bearing phases counted. Not only would the time impact the statistical significance of sample interpretation, but it would limit the total number of samples one could study, thus the representativeness of the data to the site.

A number of phases for both lead and arsenic are considered stoichiometric. These include the following:

Galena (PbS)
Lead Oxide (PbO)
Native Lead (Pb)
Cerussite ($PbCO_3$)
Anglesite ($PbSO_4$)
Crocoite ($PbCrO_4$)
Alamosite ($PbSiO_3$)
Lead Arsenate ($PbAsO$)
Arsenolite (As_2O_3)
Realgar (AsS)
Orpiment (As_2S_3)
Arsenopyrite ($AsFeS$)

The author is aware that these are not all strictly stoichiometric phases. As an example, "lead oxide" would include; litharge (PbO), massicot (PbO), minium (Pb_3O_4, plattnerite (PbO_2), and scrutinyite (αPbO_2). In addition, phases such as lead hydroxide, lead isobuyrate, lead lactate, lead laurate, lead malate, lead oxalate and even lead nitrate would be grouped in this category. The phase "lead arsenate" would include; schultenite ($PbHAsO_4$), paulmooreite ($Pb_2As_2O_5$) as well as all the meta/ortho arsenate/arsenite phases. With very careful EMPA analyses most of these phases could be isolated; however, as the data is currently used this effort is not taken unless the client request further work.

The remaining phases that are commonly identified are far more generic. The concentration of the metal(s) of interest in these phases are thus variable and require site-specific estimates of there concentration values. These are obtained for each project by randomly collecting EMPA quantitative analyses (for lead or arsenic) for these phases and calculating average values. For these phases the first criteria used in identification is to determine if the phase is either; an oxide, carbonate, sulfide, sulfate, or phosphate. Secondly, with the exception of the "phosphates", the major cation associated with the phase is further identified. Therefore, phases such as Fe-sulfate, FeOOH, MnOOH, PbMO, AsMO, or $PbMSO_4$ are identified. Some of these phases could represent a stoichiometric mineral forms such as allactite $Mn_7(AsO_4)_2(OH)_8$, plumbojarosite $PbFe_6(SO_4)_4(OH)_{12}$, plumboferrite $PbFe_4O_7$, carminite $PbFe_2[OHAsO_4]_2$, nelenite $(Mn,Fe)_{16}Si_{12}As_3O_{36}(OH)_{17}$, or quenselite $PbMnO_2(OH)$; however, it is the authors belief that most of these phases are metastable and/or amorphous and have some quantity of arsenic and/or lead sorbed to their surface.

The "phosphate" group is even more generic in that the only common dominant ion is PO_4. There are many crystalline forms of phosphate that contain lead such as; pyromorphite $Pb_5[Cl(PO_4)_3]$, plumbogummite $PbAl_3(PO_4)_2(OH)_5$-H_2O, orpheite $PbAl_3[(OH)_6(PO_4,SO_4)_2]$, drugmanite $Pb_2(Fe,Al)(PO_4)2OH$-H_2O, and corkite $PbFe_3[(OH)_6\ SO_4\ PO_4]$. Although arsenic and phosphorous are considered competitive, a number of arsenic-bearing phosphates have been identified; walentaite $(Ca,Mn,Fe)Fe_3(AsO_4,PO_4)_4$-$7H_2O$, morelandite $(Ba,Ca,Pb)_5\ Cl[AsO_4,PO_4]_3$, and turneaureite $Ca_5(Cl)[(AsO_4,\ PO_4)_3]$. As with previous phases, careful EMPA analyses could isolated the complete stoichiometry; however, as the data is currently used this effort is not taken unless the client request further work.

Since the chemistry and/or sorption capacity of these categories are quite variable one should be careful in ascribing RBA (relative bioaccessability) to these metal forms. In particular, if sorption is the primary factor controlling the presence of arsenic or lead, factors such as temperature, redox, and pH can influence the metal stability significantly. However, if particle size and morphology (liberated-included) are similar, it appears, primarily from in vitro studies, that iron oxides and sulfates tend to be less bioaccessable than manganese oxides and phosphates.

Birks, L.S., 1971, Electron Probe Microanalysis, 2nd Ed., New York: Wiley-Interscience.

Heinrich, K.F.J., 1981, Electron Beam X-ray Microanalysis. New York. Van Nostrand.

As stated previously, a maximum of 8 hours will be spent in scanning and analyzing each mount. For most speciation projects the goal is to count between 100-200 particles. In the event that these goals are achieved in less than 8 hours, particle counting may continue or the analyst may move to another sample in order to increase the sample population.

10.4 Quantitative Analyses

Quantitative analyses are required to establish the average metal content of the metal-bearing minerals, which have variable metal contents as: Iron-(M) sulfate, Iron-(M) oxide, Manganese-(M) oxide, organic, and slag. These determinations are important, especially in the case of slag, which is expected to have considerable variation in their dissolved metal content.

Results will be analyzed statistically to establish mean values. They may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the later case, non-parametric statistics may have to be used or the median value has to be established.

Associations

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes.

10.5 Instrument Calibration and Standardization

The WDS will have spectrometers calibrated for the metal of concern, carbon, oxygen and sulfur on the appropriate crystals using mineral standards. The EDS will have multi-channel analyzer (MCA) calibrated for known peak energy centroids. Calibration will be performed so as to have both low (1.0-3.0 KeV) and high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

The magnification marker on the instrument will be checked once a week. This will be performed by following manufacturer instructions or by measurement of commercially available grids or leucite spheres. Size measurements must be within 4 microns of certified values.

Initial calibration verification standards (ICVs) must be analyzed at the beginning of each analytical batch or once every 48 hours, whichever is more frequent. A set of mineral or glass standards will be run quantitatively for the metal of concern, sulfur, oxygen and carbon. If elemental quantities of the ICVs do not fall within +/- 5% of certified values for each element, the instrument must be recalibrated prior to analysis of investigative samples.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI. Once a particle is isolated with the backscatter detector, a 5-second EDS spectra is collected and peaks identified. The count rates for the metal(s) of concern, sulfur, carbon and oxygen can be either visually observed on the wavelength spectrometers or K-ratios calculated.

10.6 Documentation

Photomicrographs must be taken for each sample, at a rate of 5% (1 photograph per 20 particles counted), for a maximum of 10 per sample and submitted with the results. Any additional photographs should be labeled as "opportunistic".

A positive black and white film (Polaroid 52) will be used or a 128x128 (minimum) binary image in ".tif" format may be stored. Recorded on each photomicrograph and negative will be a scale bar, magnification, sample identification , date and phase identification.

11.0 PERSONAL HEALTH AND SAFETY

Each individual operating the electron microprobe instruments will have read the "Radiation Safety Handbook" prepared by the University and follow all State guidelines for operation of X-ray equipment.

Latex gloves and particulate masks will be worn during preparation of sample cups. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

12.0 FINAL REPORT

A final laboratory report will be provided to the Contractor. The report will include all EMP data including summary tables and figures. Individual sample data will be provided on disk.

Speciation results will include: 1) a series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit; (Figure 11.0A) 2) summary histograms of metal phases identified for each waste type; (Figure 11.0B. Representative photomicrographs or .tif images will also be included in the final report (Figure 11.0C).

13.0 REFERENCES

Bornschein, R.L., P.A. Succop, K.M. Kraft, and C.S. Clark. 1987. Exterior surface lead dust, interior lead house dust and childhood lead exposure in an urban environment. In D.D. Hemphil, Ed., Trace Substances in Environmental Health XX Proceedings of the University of Missouri's 20th Annual Conference. June 1986, pp 322-332. University of Missouri, Columbia, MO.

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Emmons, S.F., J.D. Irving, and G.F. Loughlin. 1927. Geology and Ore Deposits of the Leadville Mining District, Colorado. USGS Professional Paper 148.

Davis, A., J.W. Drexler, M.V. Ruby, and A. Nicholson. 1993. The micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environ. Sci. Technol.* (In Press).

Mosimann, J.E. 1965. Statistical methods for the Pollen Analyst. In: B. Kummel and D. Raup (EDS.). *Handbook of Paleontological Techniques.* Freeman and Co., San Francisco, pp. 636-673.

Ruby, M.V., A. Davis, J.H. Kempton, J.W. Drexler, and P.D. Bergstrom. 1992. Lead bioavailability: Dissolution kinetics under simulated gastric conditions. *Environ. Sci. Technol.* 26(6): pp 1242-1248.

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Table 2-1

Common Metal-Bearing Forms Found Within Mining, Smelting, Agricultural, Industrial and Residential Media

OXIDES

- Lead Oxide
- Manganese (metal) oxide
- Iron (metal) oxide
- Lead molybdenum oxide
- Arsenic (metal) Oxide
- Lead (metal) Oxides
- Cadmium Oxide
- Copper Oxides
- Zinc Oxide
- Lead Arsenate
- Arsenic Trioxide
- Calcium (metal) oxide

SILICATES

- Slag
- Lead silicate
- Arsenic silicate
- Zinc silicate
- Clays

SULFATES

- Iron (metal) sulfate
- Lead sulfate
- Lead barite
- Zinc Sulfate
- Arsenic sulfate
- Copper sulfate

CARBONATES

- Lead Carbonate
- Zinc Carbonate

PHOSPHATES

- (metal) phosphates

SULFIDES

- Lead sulfide
- Sulfur-containing salts
- Iron-arsenic sulfide
- Zinc sulfide
- Copper sulfides
- Copper-iron sulfide
- Cadmium Sulfide

OTHER

- Native: Lead, Copper, Cadmium, Mercury, Indium, Thallium, Selenium
- Lead/Arsenic/Cadmium/Mercury Chlorides
- Paint
- Solder
- Organic lead
- Lead vanadate
- Minor telluride, and bismuth-lead phases

Figure 10.1

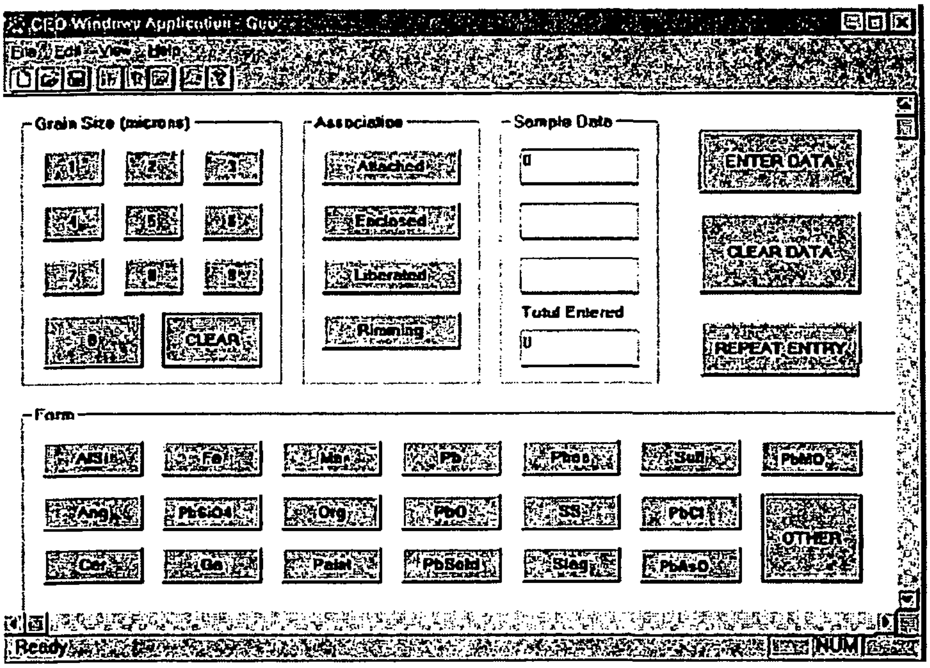

Grain Size (microns)
Association
Sample Data
ENTER DATA
1
2
3
Attached
4
5
6
Enclosed
CLEAR DATA
7
8
9
Liberated
Total Entered
0
CLEAR
Rimming
REPEAT ENTRY
Form
Fe
Pb
PbMO
Org
PbO
SS
PbCl
OTHER
Paint
PbSold
Slag
PbAsO
Ready
NUM

Table 10-1

EMP Standard Operating Conditions

	WDS	EDS
Accelerating Voltage	15 KV	15-20 KV
Beam Size	1-2 microns	1-2 microns
Cup Current	10-30 NanoAmps	10-30 NanoAmps
Ev/Channel	NA	10 or 20
Stage Tilt	NA	Fixed
Working Distance	**NA**	Fixed
MCA time Constant	NA	7.5-12 microseconds
X-ray lines	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET **As L-alpha TAP** **Cu K-alpha LIF** Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF In L-alpha PET Tl L-alpha LIF Hg L-alpha LIF Se L-alpha LIF Sb L-alpha PET	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV In L-alpha 3.28 KeV Tl M-alpha 2.27 KeV Tl L-alpha 10.26 KeV Hg L-alpha 9.98 KeV Hg M-alpha 2.19 KeV Se L-alpha 1.37 KeV Sb L-alpha 3.60 KeV

Figure 11.0A

Lead Form	#Particles	Mean-Size microns	Std-Dev	Range low microns	Range high microns
total	147	9.27	13.07	1	80
FeOOH	16	21.81	21.86	7	80
Cerussite	42	11.24	12.84	1	50
ZnMO/CO3	74	3.53	2.29	1	12
FeSO4	5	23.6	19.73	7	48
Galena	10	16.3	16.45	2	50

Form	**F** %	**F-Bio** %	**Rm** %	**BioRm** %	**Error-95%**	**Mean Particle Size** Microns
FeOOH	11.71	65.9	24.77	26.22	9.75	13.27
Anglesite	0	0	4.27	0	1.06	4
Cerussite	0	0	1.27	0	0.53	1
Slag	87.64	0	0	0	8.03	290
MnOOH	0.65	32.66	54.22	57.4	8.5	7.95
Galena	0	0.76	12.88	13.64	1.5	8
Phosphate	0	0.67	2.59	2.74	1.4	3.5

Figure 11.0B

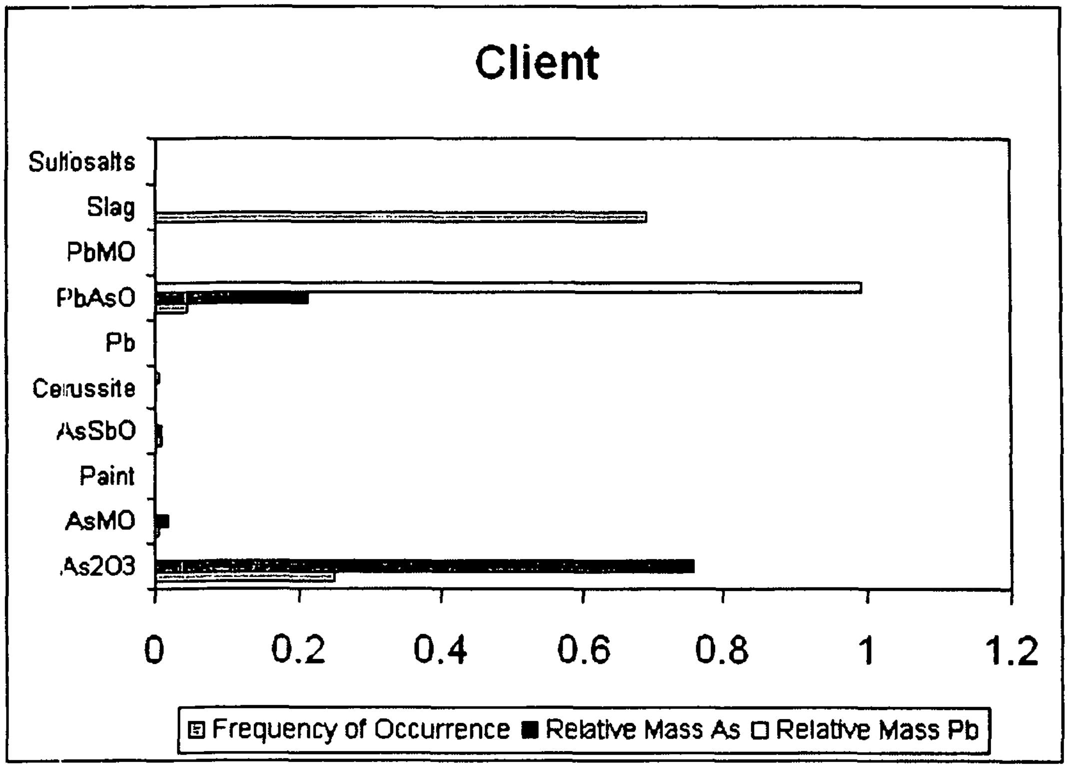
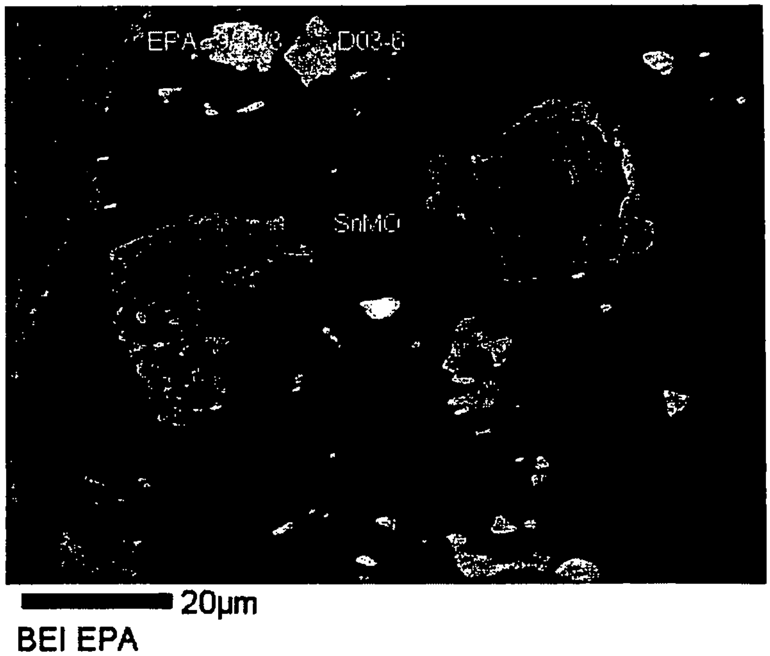
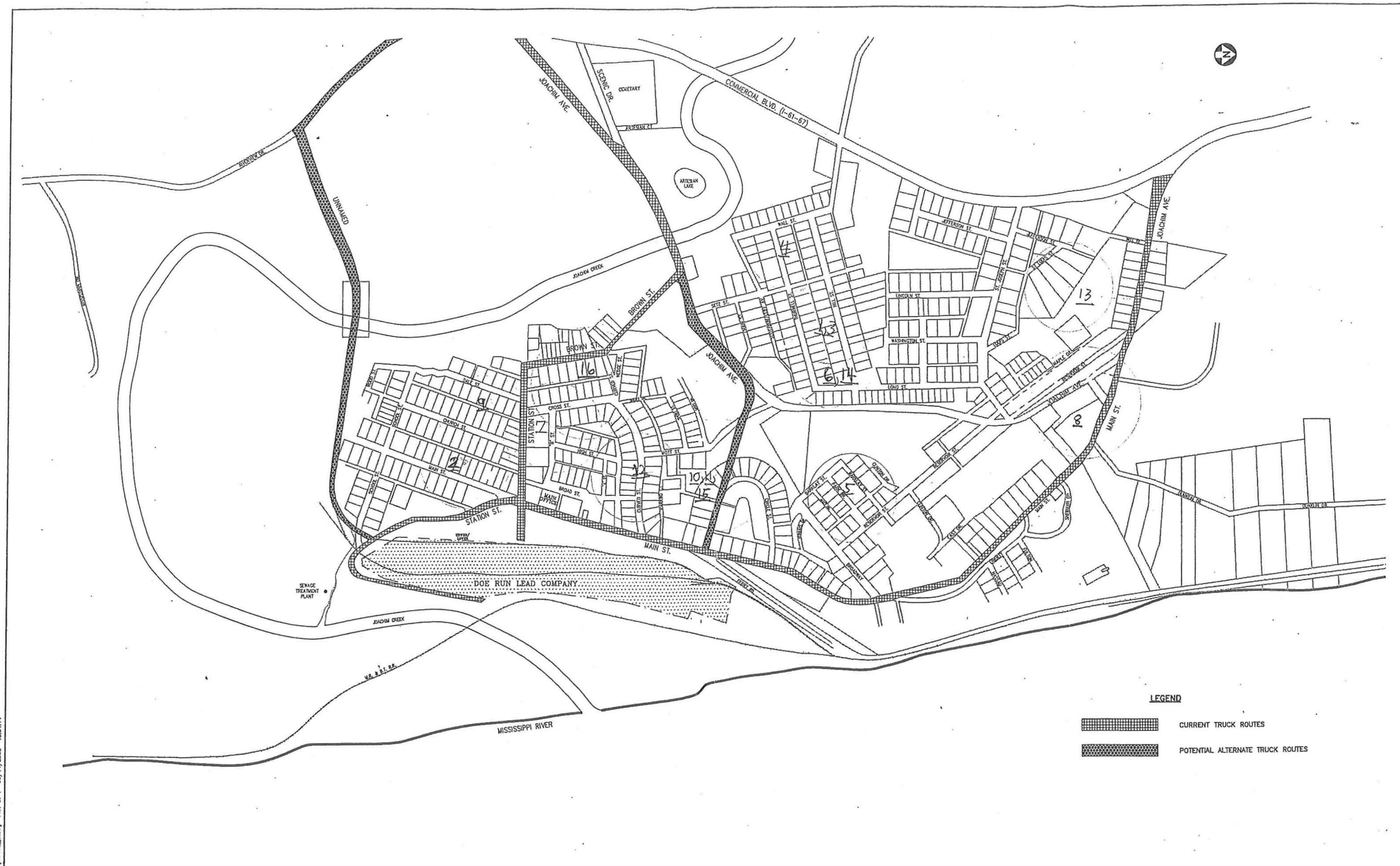

Client
Sulfosalts
Slag
PbMO
PbAsO
Pb
Cerussite
AsSbO
Paint
AsMO
As2O3
0
0.2
0.4
0.6
0.8
1
1.2
Frequency of Occurrence
Relative Mass As
Relative Mass Pb

Figure 11.0C





NO.	BY	CHK	APP	DATE	REVISION DESCRIPTION

CLIENT / BID / CONSTRUCTION

RELEASED TO/FOR: A B C 0 1 2 3 — DATE RELEASED

BARR

Project Office:
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Fax: (573) 638-5001
www.barr.com

Corporate Headquarters:
Minneapolis, Minnesota
Ph: 1-800-632-2277

Scale	NTS
Date	3/22/02
Drawn	SDL
Checked	
Designed	
Approved	

THE DOE RUN COMPANY
HERCULANEUM, MO

DESIGNATED TRUCK TRAFFIC ROUTES

FIGURE 3

BARR PROJECT No. 25/51-018
CLIENT PROJECT No.
DWG. No.
REV. No.

M:\cad\25510180\FIGURE_3.dwg Plot at 1 05/14/2002 13:54:14